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Large Area Growth of Cubic Silicon Carbide Using Close Space PVT by Application of Homoepitaxial Seeding

M. Kollmuss[1a*], M. Schoeler[1b], R. Anzalone[2c], M. Mauceri[3d], F. La Via[4e], P. Wellmann[1f]

[1]Crystal Growth Lab, Materials Department 6 (i-meet), FAU Erlangen-Nürnberg, Martensstr. 7, D-91058 Erlangen, Germany

[2]STMicroelectronics, stradale Primosole 50, 95121 CATANIA, Italy

[3]LPE S.P.A., Sedicesima Strada, 95121, Catania, Italy

[4]CNR-IMM, sezione di Catania, Stradale Primosole 50, I-95121 Catania, Italy

[a]manuel.kollmuss@fau.de, [b]michael.schoeler@fau.de, [c]ruggero.anzalone@st.com, [d]Marco.Mauceri@lpe-epi.com, [e]francesco.lavia@imm.cnr.it, [f]Peter.wellmann@fau.de

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Abstract. One setback that hinders the breakthrough of cubic silicon carbide is the lack of suitable seeding material for sublimation growth methods such as PVT. We present the growth of large area cubic silicon carbide material, up to a diameter of 100 mm, with a sublimation growth process called close spaced PVT (CS-PVT). Freestanding 3C-SiC seeding layers were grown by a homoepitaxial CVD process. Subsequently CS-PVT was used to grow crystals up to a thickness of 1 mm. To prevent backside sublimation a carbon containing layer was applied as protection. Due to the presence of a wafer bow as well as a rough backside of the used seeds additional effort was necessary to apply the coating. After growth no visible curvature was present independent of the grown layer thickness and sample size. Raman spectroscopy was performed on the seeds and grown crystals, showing that the overall stress level of the material was reduced by CS-PVT.

Introduction

Large area growth of hexagonal polytypes of silicon carbide (4H-SiC and 6H-SiC) up to diameters of 150 mm using physical vapor transport (PVT) can be considered mature. In fact, the first wafer production with a diameter of 200 mm has been implemented. Meanwhile the same cannot be said for the cubic polytype (3C-SiC). The growth of this polytype is mainly hindered by a lack of suitable seeding material as a starting point for sublimation growth processes. Nevertheless, progress was made in recent years regarding this problem. Schuh et al. [1] showed that thin 3C-SiC layers fabricated by heteroepitaxial chemical vapor deposition (CVD) on silicon can be used to prepare a seeding stack suitable for high temperature growth processes. Crystals with reasonable size and thickness could be grown using this method [2, 3]. However, cracking of the thin 3C-SiC layers during seed preparation limited the achievable diameter. A promising new seeding material has become available due to ongoing research in the field of CVD growth of 3C-SiC. Anzalone et al. [4] described the production of freestanding 3C-SiC wafers grown by homoepitaxial CVD at elevated temperature. Using such seeding material for sublimation growth processes offers new possibilities for the growth of large area cubic silicon carbide. A suitable sublimation process for 3C-SiC is the close space PVT (CS-PVT) which is also referred to as sublimation sandwich. In this work we present the growth of freestanding 3C-SiC crystals up to diameters of 100 mm on homoepitaxial grown 3C-SiC seeds using CS-PVT. Remaining problems as well as the possibilities of this approach are discussed. Additionally, the potential of the presented approach towards the growth of 150 mm 3C-SiC crystals will be presented.

Experimental

CS-PVT growth was carried out in a state-of-the-art PVT reactor using a sandwich like hot zone to reach the required growth conditions for stable growth of cubic silicon carbide. A Tantalum foil acting as a carbon getter was placed underneath the source to maintain a silicon rich gas phase. The distance between the source and the seed was kept small (gap size 1 mm) by a graphite spacer to achieve a high vertical temperature gradient. The high supersaturation suitable for the cubic polytype goes along with the temperature gradient and is also achieved by a fast heat up of the system (40 K/min). Poly- or monocrystalline SiC wafers were used as source material while free-standing, (100) oriented 3C-SiC layers provided by LPE Epitaxial Technology Center in Catania were used as seeds. The seeds had a tilt of 4° towards [110], a diameter of 150 mm and a thickness of 200-235 µm. A laser ablation process was used to remove the defect-rich edges of the seeds and to cut the seeds to a sample size of either 50 mm or 100 mm. To protect the backside of the seeds during sublimation growth a carbon containing coating was applied. As the used seeds contained a wafer bow the application of this backside coating was done manually and will be described later. CS-PVT growth was conducted at temperatures between 1970 and 2070°C under vacuum conditions with vertical temperature gradients between 4 and 8 K/mm resulting in growth rates between 90 and 230 µm/h. After the sublimation growth the backside protection layer was removed by oxidation. The growth setup and the hot zone used is also described in [5, 6]. For the optical characterization of the grown crystals an Epson perfection v800 flat-bed scanner with a maximum resolution of 6400 dpi was used. Raman measurements were conducted using a Horiba LabRAM HR Evolution confocal Raman microscope with a laser wavelength of 532 nm, a power of 3.19 mW power at an optical resolution of 50x and a grating of 1800 gr/mm.

Results and Discussion

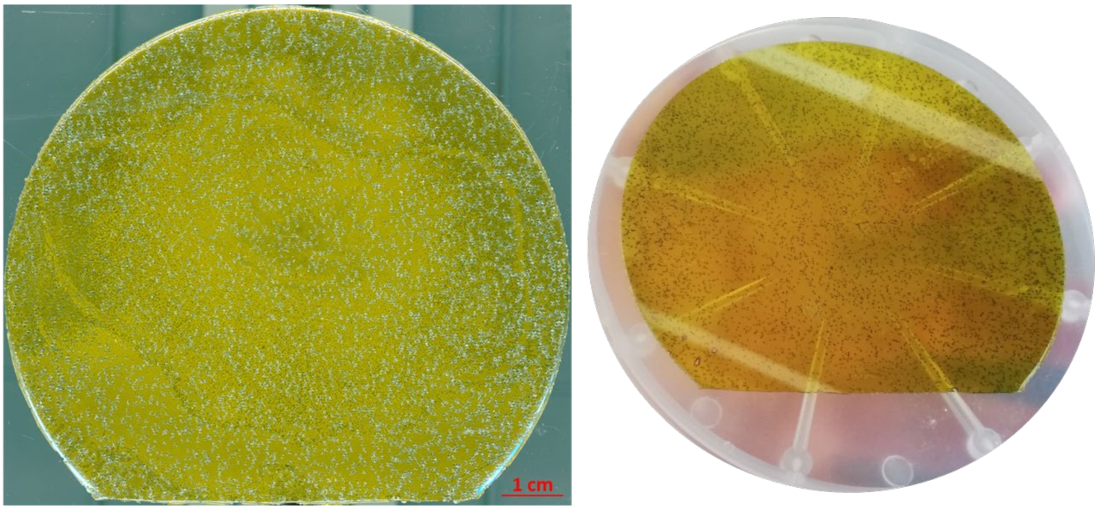

Fig. 1: Left: High resolution scan of freestanding 3C-SiC crystal grown by CS-PVT with a diameter of 92 mm and a thickness of 650 µm. The flat is the result of layer breakage during seed preparation. The darker area stems from the rough backside of the seed used. Right: Photography of same crystal after optical polishing on front- and backside resulting in a specular appearance.

Growth of freestanding large area material. Fig. 1 shows the results for the growth on a seed with a diameter of 100 mm. The resulting crystal had a diameter of 92 mm due to the used graphite spacer and had a thickness of 650 µm. The crystal exhibits the yellow color typical for the cubic polytype of silicon carbide and has a smooth growth front. The polytype was also confirmed by Raman measurements, as no other peaks were observed besides those characteristic for 3C-SiC. During the seed preparation cracking of the bowed seed occurred during the removal of the defect rich edges of the seed, leading to the visible flat. Laser ablation will not cut through the whole seed once the thickness reaches values higher approx. 200 µm. Thus, a slight mechanical force has to be applied to separate the seed edges which, together with the present bow and remaining stress in the seed, can result in cracking. The freestanding area of the layer is approximately 60 cm^2. To our knowledge this marks the first time a freestanding 3C-SiC crystal with such size and thickness was grown. The bow of the used seed wafer vanished during the sublimation growth and will be discussed in the next section. Due to flattening it was also possible to do optical polishing of the crystal on the front as well as the backside resulting in a specular surface as it can be seen in Fig. 1 (right).

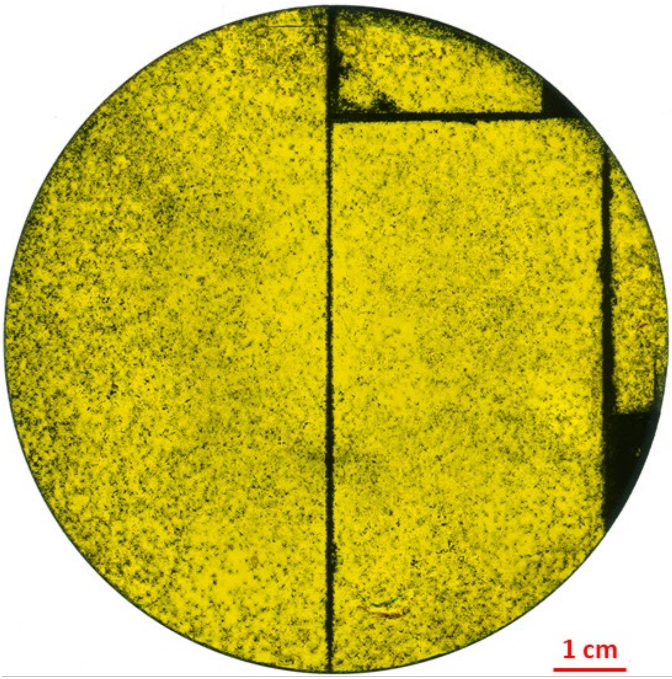

Fig. 2: High resolution scan of cracked, freestanding 100 mm 3C-SiC crystal grown by sublimation growth on a seeding stack. The manufacturing of the seeding stack is described in [2, 5]. Multiple cracks can be seen in the crystal showing the limitation of the seed transfer used.

Another approach for the sublimation growth of 3C-SiC is mentioned in [2, 5]. Prior to the growth a seeding stack needs to be produced from a thin 3C-SiC layer grown on silicon by heteroepitaxial CVD. During this transfer process the silicon is etched away. However, the handling of the freestanding layers as well as the etching itself, comes with a high risk of layer cracking. The cracking probability will increase with increasing layer size and limits the scale up potential. An example for the sublimation growth on seeding stacks produced by this transfer can be seen in Fig 2. Compared to the crystal in Fig. 1 multiple cracks are clearly visible showing the limitations for large area growth. In contrast the approach used in this work showed a significant lower probability of seed cracking. Therefore, a reasonable potential for upscaling towards larger diameters can be associated. An improvement in the seed quality should reduce the chance of cracking. Laser ablation could become even redundant, if the defect density at the seed edges is further decreased. This would allow the growth of crystals with larger diameters using sublimation growth.

Reduction of wafer bow during CS-PVT. Fig. 3 shows a comparison between the freestanding seed and the resulting crystal after CS-PVT for a 50 mm growth run. The visible bow in the left-hand figure is typical for the used seeds. These layers still suffer from a bowing up to 4 mm for a 150 mm wafer. In this context, bow refers to the deviation between the seed or crystal center and a reference plane defined by the edges of the sample. The bow of the seed in Fig. 3 has a value of approx. 0.5 mm. During the sublimation growth this bow completely vanished, resulting in a flat 3C-SiC crystal. This phenomenon was observed for all experiments carried out, regardless of the sample diameter and the grown layer thickness, which was between 0.5 and 1 mm. To further understand this effect a seed was heated up to the same temperature as during growth runs. Instead of vacuum an argon atmosphere at 800 mbar was applied to suppress sublimation of SiC in the growth cell thus, checking if the bow reduction can be induced by a heat treatment alone. As no reduction of the bow could be observed, the reduction mechanism must be induced by the material grown on top of the seed during CS-PVT.

Raman spectroscopy was used to evaluate the stress level in the samples before and after sublimation growth. The peak position of the transversal optical mode was used. For a stress-free crystal, the value of the peak should be at a Raman shift of 796 cm^{-1} [7]. Due to internal stress of the crystal lattice the position will shift to lower values or higher values for tensile or compressive stress, respectively. The measurements showed that the values for all samples were closer to the stress-free value after the sublimation growth. Therefore, not only a reduction of the sample bow but also a reduction of the overall stress inside the sample was achieved by CS-PVT. This is in good agreement with the results of Schuh et al. [2]. They also observed a stress reduction during sublimation growth. Although, they used a different type of seeding material, it shows the potential of the sublimation growth processes for stress reduction in silicon carbide crystals. This is important as the influence of stress and its handling becomes more pivotal with increased crystal size.

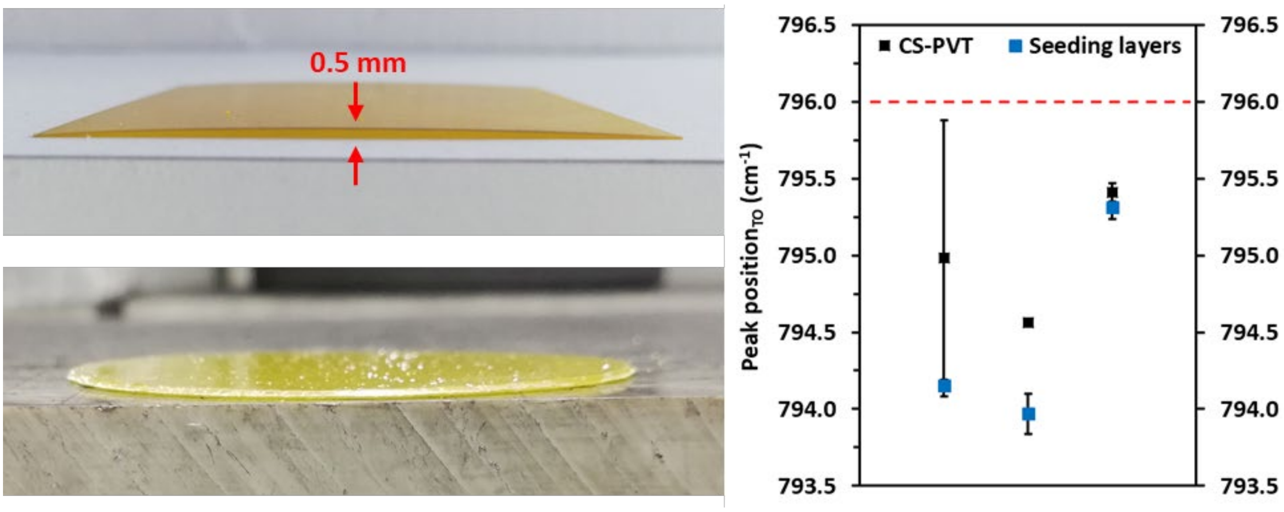

Fig. 3: Left: Seed (upper) and crystal after the CS-PVT growth (lower) for a 50 mm sample. The clearly visible bow of the seeding layer completely vanished during the sublimation growth (bottom). Right: Peak position of the TO-Mode of Raman spectroscopy for seeding layers (blue) and associated crystals grown by CS-PVT. For all samples a reduction of the stress towards the stress-free value of 796 cm^{-1} could be observed (red dotted line).

Backside protection. Currently there are two main challenges regarding the backside protection of the seeding layers used: the bow and a rough backside. Besides the risk of seed breakage, bow also complicates the application of backside protection since processing methods like spin coating can´t be used. Therefore, a more manual approach was used. First the backside of the seed was covered completely with a carbon containing liquid coating and afterwards the seed was placed vertically to allow the excess material to drain off. Subsequently, a high temperature annealing under vacuum conditions was performed to cure the coating. The rough backside of the seeds has its origin in the fabrication of the layers. The initial CVD growth step is done on silicon. Afterwards the silicon is removed by an in situ melting process inside the CVD reaction chamber [8]. During this step the backside of the grown 3C layer is damaged leading to surface roughening [9]. This roughness can hamper the adhesion of the backside protection layer during the sublimation growth. Therefore, the right choice of processing parameters plays a crucial role. Coatings that are too thick can delaminate during vapor phase growth processes whereas layers that are too thin can lead to insufficient protection. In both cases backside sublimation will occur, limiting the process window for sublimation growth.

Summary/Outlook

We showed that homoepitaxial 3C-SiC layers can be successfully used for large area bulk growth of freestanding 3C-SiC crystals by CS-PVT. Crystals up to nearly 100 mm could be grown with thicknesses up to 1 mm. During the growth the remaining bow in the seeding layers vanish and, additionally, the stress level of the samples can be reduced. To protect the crystal from backside sublimation during the growth runs a carbon containing coating was applied. However, the bow of the seeds as well as the rough backside made additional efforts necessary regarding the coating process. Compared to seeding material used in other works for sublimation growth of cubic silicon carbide, this approach showed a higher overall scale up potential, bringing the goal of 150 mm cubic silicon carbide bulk crystals within reach.

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