Sublimation epitaxy of cubic silicon carbide in vacuum

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Abstract. The epitaxial growth was compared of cubic silicon carbide on 6H-SiC substrates prepared in four different ways: (i) as received, (ii) re-polished, (iii) annealed and subsequently covered by a Si layer, (iv) with a (111) 3C-SiC buffer layer. The morphological details of the grown layers were studied by optical microscopy and their structure, by transmission electron microscopy. The influence of the substrate on the nucleation of 3C-SiC, on the homoepitaxial 6H-SiC nucleation before 3C-SiC and on the defect formation, primarily twinning, is discussed.

1. Introduction

Silicon carbide has long been considered a promising semiconductor for high-temperature, high-power and high-frequency radiation-resistant device applications. The most common SiC polytypes (one-dimensional polymorphic modifications) are the two hexagonal ones, 4H-SiC and 6H-SiC, as well as the 3C-SiC, which is the only one exhibiting isotropic properties due to its cubic structure. Additionally, 3C-SiC is regarded advantageous over the other more hexagonal polytypes because it shows the highest electron mobility and lower density of the near-interface-traps in the SiO2/3C-SiC system due to the smaller band gap. A crucial problem hindering the future development of a 3C-SiC technology is the unavailability of 3C-SiC substrates. Frequently, in order to overcome problems related to mismatch, as in the case of Si, the growth is performed on substrates from a hexagonal polytype (4H- or 6H-SiC). In this case, the 3C-SiC nucleates spontaneously on (0001) surfaces if the temperature is below 2000°C [1].

Efficient transport of the Si- and C-bearing species resulting in fast epitaxy is also obtained by implementing growth under vacuum at a short distance between the source and the substrate. Under such conditions, the growth rate is high (up to 1 mm/h for 3C-SiC) and the rate limiting mechanism in the growth configuration for sublimation epitaxy is the sublimation of the solid SiC source material. The use of a monolithic SiC plate gives more uniform sublimation than the traditional SiC powder. Earlier studies comparing epitaxy in vacuum and in argon atmosphere [2] found that the growth rate decreases by an order of magnitude at around 1–10 mbar argon pressure and the molecular vapors diffusion becomes the rate-determining step at higher vapor pressures.
Supersaturation is also dependant upon the medium (vacuum, argon, hydrogen or helium). Supersaturation certainly occurs since the Si/C ratio changes, as judged from the observation of step-bunching in sublimation epitaxy of 6H- and 4H-SiC [3].

The 3C-SiC is best formed under high Si/C ratio and high supersaturation conditions [4]; the best choice is, therefore, growth under vacuum conditions. The present paper presents investigation on the formation of 3C-SiC grown in vacuum on differently treated 6H-SiC substrates.

2. Experimental
The samples were grown in a vertical quartz tube reactor [2]. The cylindrical graphite growth cell consisted of a bottom piece and a lid mounted inside thermally insulating graphite foam heated by an inductive coil using an RF generator. Growth was performed in vacuum (pressure ~10⁻⁵ mbar). The source and the substrate were separated by a graphite spacer at a distance of 1 mm. A polycrystalline 3C-SiC plate was used as a source. When a temperature gradient is applied, with the temperature of the source being higher than that of the substrate, Si- and C-containing species are sublimed from the source and transported to the substrate where SiC nucleates.

The substrates used were subjected to different treatment prior to the growth experiment. Results were compared for (i) as received 6H-SiC substrates, (ii) 6H-SiC substrates re-polished by NovaSiC to minimize surface roughness; (iii) substrates annealed in a CVD reactor at 1450 °C for 10 min to reveal the growth steps and subsequently covered by a Si layer to protect the steps from the environment [5]; (iv) substrates with a 1.5 μm 3C-SiC buffer layer grown by means of the vapor-liquid-solid (VLS) method using a Si–Ge melt [6]. The entire set of growth experiments was performed on the Si-face of on-axis (0001) 6H-SiC substrates at identical conditions: growth temperature 1775 °C, growth duration 30 min, and a temperature ramp of 5 K/min. The 3C- or 6H-SiC polytypes were identified by means of optical microscopy with Nomarski interference contrast, photoluminescence imaging at 77 K, and Fourier transform infrared spectroscopy. The structural quality of the layers was studied by transmission electron microscopy (TEM) in cross-section and plane-view configurations. The observations were performed on a JEOL 100X conventional TEM at acceleration voltage of 100 kV.

3. Results and discussion
In general, one can expect that the different surfaces would affect growth and nucleation in different ways. Rougher surfaces would act as nucleation sites for 6H-SiC instead of favoring formation of 3C-SiC, and smoother surfaces would favor formation of more 3C-SiC centers as these are usually created by two-dimensional island formation on smooth surfaces [7], i.e. would result in a larger percentage of 3C-SiC on the substrates. However, there was no significant difference between the layers grown on as-received and on re-polished substrates (which had smoother surfaces which should have favored 3C-SiC formation), the coverage of 3C-SiC compared to 6H-SiC was ~ 87 % in both cases. Thus, the surface smoothes does not influence noticeably the 3C-SiC nucleation. This observation suggests that during the temperature ramp up there is initial homoepitaxial 6H-SiC growth that creates perfectly on-axis regions (making large enough terraces for two dimensional nucleation instead of nucleation at steps which would replicate the 6H-SiC substrate), which is very important for the 3C-SiC formation [7,8].

Growth on annealed and silicon covered substrates showed less nucleation of 3C-SiC (~45 % only). The annealing is performed to create steps, which favor 3C-SiC growth during the VLS process [5]. In the VLS process, the 3C-SiC starts to nucleate at the terraces of these steps. However, in vapor phase growth, the steps enhance growth at the ledges and, thus, reproduction of the 6H-SiC substrate polytype, as proved by the lower percentage of 3C-SiC when using annealed substrates. Thus the growth mechanism in this case is step-controlled, and 3C-SiC is not likely to form heteroepitaxially on 6H-SiC.

On the other hand, almost pure 3C-SiC coverage was achieved on substrates with a VLS-grown 3C-SiC layer. About 99.9 % of the layer was 3C-SiC. The temperature ramp-up [9] is thus well matched with the 3C-SiC layer, and homoepitaxial growth occurs. The surface of the sublimation grown 3C-SiC layer was improved compared to the VLS.
Figure 1. TEM micrographs of the layer grown on as-received 6H-SiC substrates. The images show the formation of (a) a fourfold twin complex, (b) interface between two twins with zigzag propagation where the facets follow the (111) and (211) planes of the twins as deduced by the corresponding diffraction pattern in (c). The reflections due to the T2 and T4 twins are indicated by an asterisk * and a circle, respectively.

The microstructure and, consequently, the crystalline quality of the grown layers was investigated by TEM. The TEM micrographs for the growth (i) on as-received 6H-SiC substrates and (ii) on buffer layer of 3C-SiC, deposited prior the sublimation by VLS, are presented in figure 1 and figure 2, respectively. The following observations can be made: (i) when growth on 6H-SiC substrates was performed, the most important defects formed in the layers under investigation were twins. As it is shown in figure 1, multiple twinning appear along all \{\{11\}\} planes. This leads to the formation of characteristic triangular defects as shown in figure 1a. They consist of four twins, denoted as T1-T4 in the figure and the twinning took place along the \{\{11\}\} planes (T1/T2 and T3/T4 interfaces) and along the \{\{122\}\} planes (T2/T3 interfaces). The \{\{11\}\} twin interfaces were always observed to be coherent as clearly seen from the images. In addition, the multiple twinning lead to interfaces with zig-zag propagation, where facets along \{\{11\}\} and \{\{21\}\} planes are formed, which is seen in figure 1b and the corresponding diffraction pattern in 1c. The streaks in the diffraction pattern indicate the formation of SF or very thin slabs of micro-twins. It must be noted that the nucleation of the multiple fourfold complex, shown in figure 1a is not very well understood, but one can speculate by its appearance that it is predetermined by the surface pattern of the 6H-SiC substrate. In support of the latter suggestion we observed that (ii) in the layers grown when (111) 3C-SiC buffer was deposited before the sublimation epitaxy, the appearance of such multiple fourfold twins with perfectly coherent interfaces was not observed. In this case, due to the absence of selectivity from the seed, the forming twin interfaces were not coherent, which is shown in figure 2a. In addition, different domains misoriented about the [01\{1\}] zone axis were observed. This is clearly confirmed by the area which is out of contrast in figure 2a, denoted as A. For clarity, the appearance of such misoriented grains is also illustrated in figure 2b, where they are denoted by A1-A5. However, it is noteworthy that even if such defective areas were observed in the case of homoepitaxy, large areas with low defects density were also formed.
4. Conclusions

We found that almost 100% 3C-SiC could be obtained in homoepitaxial growth while conversion to 3C-SiC on 6H-SiC substrates was not fully possible. The initial nucleation in the latter case must be understood in detail regarding the two-dimensional nucleation, when 6H-SiC and 3C-SiC islands compete at the initial nucleation stage. Any steps present on the surface of the substrate will lower the formation probability of 3C-SiC.

The microstructural characterization showed the formation of coherent fourfold twins along all \{111\} planes in the layers grown heteroepitaxially on 6H-SiC substrates. In the case of homoepitaxy, the multiple interfaces between the twins were incoherent and different domains were misoriented with respect to one another. However, it is noteworthy that even if such domains were formed, the defect density was quite inhomogeneous and large areas free of defects were seen.

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