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Chemical Vapor Deposition of 3C-SiC on [100] Oriented Silicon at low Temperature < 1200°C for Photonic Applications

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Abstract. 3C-SiC films have been grown on [100] n-doped Si substrates in a horizontal cold wall CVD reactor. Without the use of plasma enhancement, the precursors silane and propane are used to deposit silicon carbide films at T < 1200°C. The structure of the grown films has been investigated via FESEM, XRD and Raman spectroscopy. It has been found that the growth rates are between 200 and 300 nm/h. Additionally, structural analysis give evidence of polycrystalline phases. Reasons for that could be insufficient cracking of the precursors and homogenous nucleation of Si species in the gas phase.

Introduction

In the evolving field of photonic applications SiC plays an important role. The unique optical properties which are related to a wide bandgap, a high third-order optical nonlinearity and a high refractive index, make SiC a promising material for applications such as frequency combs [1]. Additionally, the CMOS compatibility of SiC makes it an even more attractive material regarding the development of optical devices [2]. Based on 3C-SiC and 4H-SiC, frequency combs were already investigated and show a high potential in the field of photonic applications [1, 3]. Combining SiC with an underlying SiO_2 film forms a suitable refractive index contrast for frequency combs [1]. Since SiO_2 becomes thermally unstable at T > 1200°C, epitaxial growth of 3C-SiC on Si at T < 1200°C is of particular interest, because it would pave the way to heteroepitaxial growth on Si-on-Insulator (SOI) substrates.

In this work 3C-SiC thin films are grown in a horizontal cold wall CVD reactor in the temperature regime below 1200°C. Without the use of a plasma the precursors propane and silane are thermally cracked in the reaction chamber to form SiC thin films on [100] oriented silicon substrates. In this temperature regime 3C-SiC is the thermodynamically most stable polytype [4]. Nevertheless, finding the right growth parameters for a high quality single crystalline SiC film in a cold wall reactor without the use of plasma is challenging. This study includes a series of 3C-SiC thin films deposited at different process parameters (variation of T and C/Si ratio) as well as structural, morphological and spectroscopic characterization.

Experimental

Substrates and epitaxial growth. The CVD experiments were carried out in the horizontal cold wall CVD reactor AIX 200/4 SiC. Silane (10 % in H_2) and propane are used as precursors and H_2 functions as carrier gas. The temperature of the inductively heated graphite susceptor is set by the power of the radio frequency power supply (Hüttinger TIG 20/300). The sample temperature is

acquired using an optical differential pyrometer. Calibration was verified by observing the melting of Germanium on Si substrate on the susceptor at 938°C. N-doped [100] Silicon Wafer pieces with the area of 2.5x2.5 cm² from SIEGERT WAFER GmbH are used as substrates. Before enclosing the substrates into the reaction chamber, they were cleaned in hot bath of acetone, following by a hot bath of ethanol and a Radio Corporation of America (RCA) cleaning step. In between those steps, the substrates were rinsed with deionized water and were dried under a nitrogen stream.

Each epitaxial process consists of several steps. Initially the reaction chamber is flushed several times with hydrogen gas to remove contaminations. Afterwards the susceptor is heated up to an elevated temperature of 800°C for a hydrogen etching step of twenty minutes at reduced pressure (20 mbar). For the carbonization step, the temperature is held at 800°C for 10 min, while the pressure is increased to 150 mbar. Consequently, a temperature ramp-up to the epitaxial growth temperature is performed. Depending on the process, the temperature and the gas flow rates are kept at the desired level during epitaxial growth for one hour before cooling down under argon flow. For the whole process the rotation of the susceptor is controlled by a gas flux beneath the susceptor. Fig. 1 depicts a typically epitaxy process.

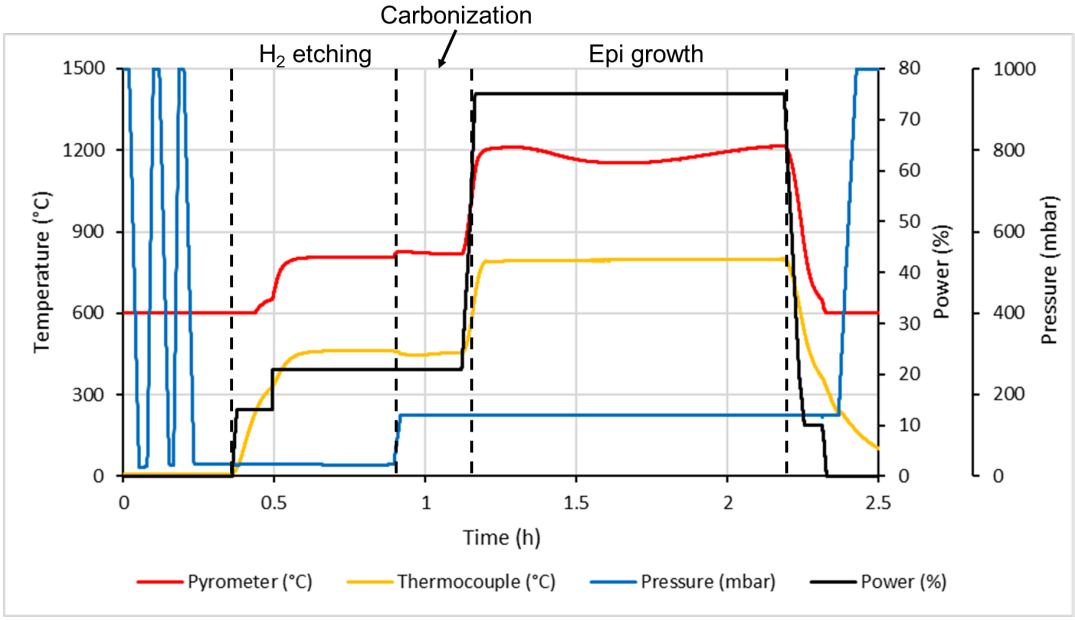

Fig. 1: Typical epitaxial growth process with hydrogen etching, carbonization and epitaxial growth.

In Table 1 two experimental growth series are listed. In the first series the temperature is variated, while the C/Si ratio is kept constant. In the second series, the C/Si ratio is variated for a constant growth temperature. The measured substrate temperature of sample E10 was slightly lower than for sample E9, E11 and E15, although the applied power of the induction heating was constant for the complete series. Sample E9 is defined as the standard process with a C/Si ratio of 6.8 and a process temperature close to 1200°C. These standard parameters are based on the work of M. Wilhelm et al. [5]. The C/Si is variated by the increase or decrease of the precursor fluxes (see Fig. 3).

Table 1: Overview of the two experimental growth series performed in this work. The mean growth temperature during epitaxial growth and the respective C/Si ratios are listed.

	Series 1 (T variation)			Series 2 (C/Si variation)			
Sample	E2	E3	E4	E9	E10	E11	E15
Temperature (°C)	1126	1153	1164	1183	1166	1183	1188
C/Si ratio	6.8	6.8	6.8	6.8	14.1	14.2	28.1

Characterization. Field effect scanning electron microscopy (SEM) (JEOL, JSM7610F) is used to analyze the surface topography and the cross section of the epitaxial thin films. The growth rate was determined using the layer thicknesses evaluated by SEM cross section image analysis. Structural analysis was carried out using X-ray diffraction (X'Pert, Philips) and Raman spectroscopy (Horiba Scientific LabRAM HR Evolution at a wavelength of 405 nm), respectively.

Results and Discussion

Fig. 2 shows topological SEM images of three samples grown at different temperatures for one hour (series 1, Table 1). The mean temperature during the epitaxial growth is indicated in the corresponding SEM images. Two main effects could be observed with increasing temperature. First the overall optical appearances of the samples changed from dull to mirror-like (no figure shown). And second the topological roughness of the layers decreases. This is attributed to a decrease of grain-like structures that will mainly form at lower temperatures on top of an underlying "closed" 3C-SiC layer. The surface coverage by these structures decreases from 82.47 % for sample E2 to 14.04 % for Sample E4. At higher temperatures (just below 1200 °C) such particles could be virtually eliminated (see Fig. 3). EDX measurements indicated that the Si/C ratio in the grains is shifted towards higher values compared to the closed 3C layers underneath. Therefore, the particles could be associated to homogenous nucleation reactions of silicon species in the gas phase [6].

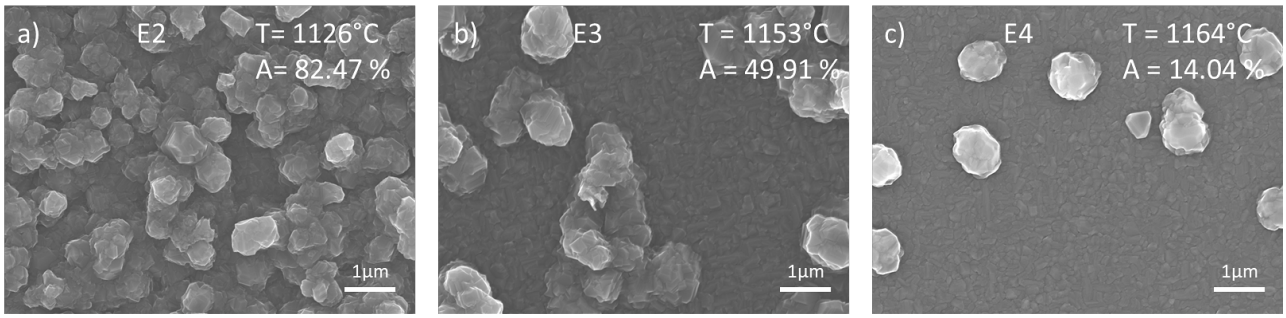

Fig. 2: SEM topography images of 3C-SiC layers grown on silicon substrates at different temperatures. The mean process temperature as well as the surface covered with grain like structures are indicated in with T and A respectively.

In Fig. 3 plan view and cross section SEM images of the four samples belonging to the experimental series 2 are depicted, where the C/Si ratio is variated by controlling the gas flows of silane and propane. For all samples no grain-like structures on top of the underlying layer are visible. Compared to the first growth series the temperatures were higher leading to a reduction of homogenous nucleation in the gas phase and therefore to an elimination of the grain-like structures. From the film thickness of the standard process a growth rate of ca. 237 nm/h can be derived. Depending on the C/Si ratio the structure of the grown films slightly changes (Fig 3). By increasing the propane flow (sample E10, Fig. 3b) in comparison to the standard process (sample E9, Fig. 3a), the topology changes to a film consisting of smaller grains. This could be due to the increased availability of carbon precursors, which could favor the formation of multiple but smaller 2D-SiC nuclei on the surface compared to lower propane flow rates. Furthermore, the growth rate increases from 237 nm/h to 301 nm/h. Meanwhile for a reduced silane flow the grain size of the grown layer is comparable to the standard process. The growth rate changes only slightly with values of 247 nm/h for sample E11 and 220 nm/h for sample E15, respectively. Chassagne et al. [7] showed, that the growth rate of SiC in a VPE reactor is mainly determined by the silane flux. In our work we found that a change in the propane flux has a higher impact while changes in the silane flow have only a small influence on the growth rate. Whereas a C/Si ratio of ca. 14 by increasing the propane flow (E10) leads to relatively small grains on the surface, a C/Si ratio of ca. 14 by decreasing the silane flow (E11) leads to comparatively bigger, merging grains. This could be explained by the lower

temperatures used in our work. While Chassagne performed epitaxial growth runs at temperatures as high as 1350 °C our experiments were limited to temperatures below 1200 °C. For lower temperatures the cracking of propane will be less efficient limiting the available carbon gas species for the SiC growth. This finding agrees with the work done by Wilhelm et al. [5].

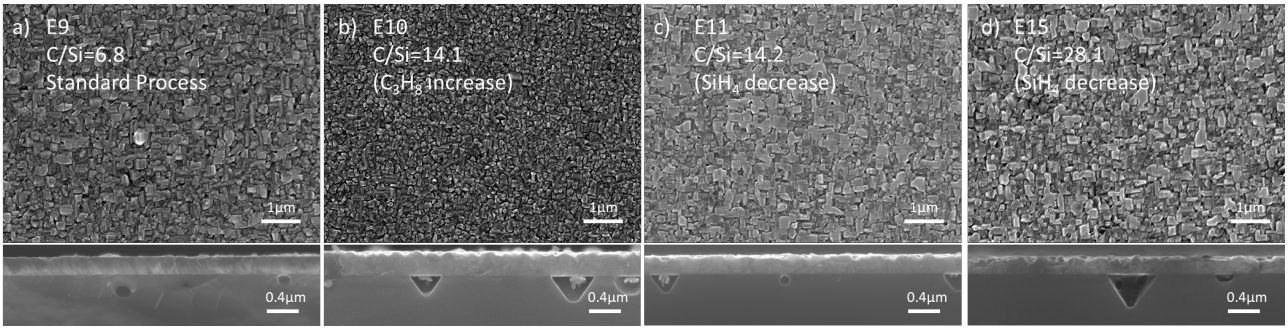

Fig. 3: SEM topography images and cross section images of samples grown in the growth series 2 with different C/Si ratio at the same temperature.

Raman spectroscopy (Fig. 5a) measurements of the samples of series 2 confirmed that the grown layers are 3C-SiC by the typically TO- and LO-peaks at around 800 cm^{-1} and 970 cm^{-1} [8], respectively. A tendency of an increase of the LO-mode peak with increasing C/Si ratio is observed. Such behavior was also observed by Wilhelm et al. and could be linked with a slightly increased layer quality [5]. Note: Also, the C/Si for sample E10 is increased the formation of smaller SiC grains due to the higher propane flow rate will lead to a reduced layer quality also evident in the higher signal of the TO-mode. Fig. 5b depicts the XRD measurement of sample E11. Next to the characteristic peaks for (200) and (400) 3C-SiC also a (311)-peak can be identified. This leads to the conclusions, that the films are not purely single crystalline. Additionally, the peak at ca 34° could be attributed to the 6H polytype. This indicates the formation of stacking faults which can generate, due to their crystallographic orientation, a signal characteristic for the hexagonal polytype.

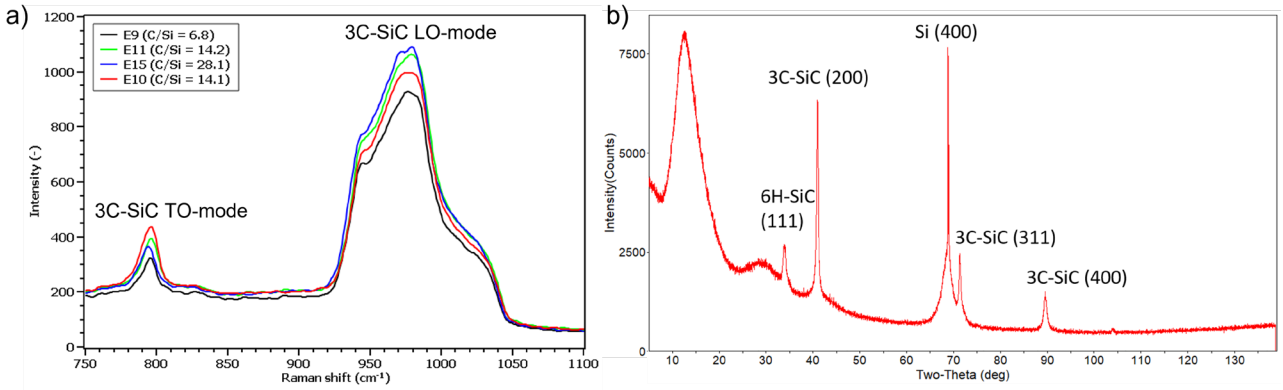

Fig. 5: (a) Raman spectroscopy results of growth series 2. (b) XRD Analysis of sample E11 with indication of SiC peaks and the (400) silicon peak (substrate). The two broad peaks at around 15° and 30° origin from the sample holder.

Cross section analyses indicate the presence of voids beneath all grown films. These voids form during the carbonization step by out-diffusion of silicon from the substrate. To avoid this effect, the carbonization step was adjusted. Therefore, the carbonization temperature is increased from 800°C to 1000°C. In addition, a silane flow of 0.3 sccm is implemented during the heat up to growth temperature. Anzalone et al. [9] showed that the addition of Si containing gas species during carbonization can reduce the void formation. Fig. 4a shows the plan view SEM of a layer grown with the adjusted carbonization step. All other growth parameters were kept constant with regard to the standard process of the growth series 2. The topography of the grown film is covered with grain-like

structures. This result and the findings from series 1 (Fig. 2) raise the assumption, that homogenous nucleation of Si species occurred during the carbonization step, which could be attributed mainly to the low temperatures. Additionally, the cross-sectional SEM image in Fig. 4b proofs, that voids could not be completely eliminated in the underlying silicon using the process described.

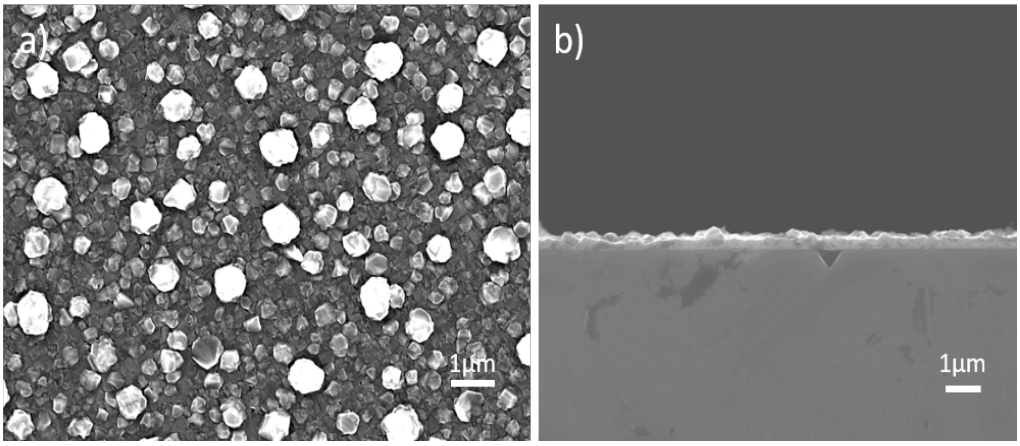

Fig. 4: (a) Topologically SEM image of a sample grown with standard parameters during epitaxial growth using elevated temperatures and a small silane flow during carbonization. (b) Cross-section SEM image of the same film, showing a void structure in the underlying silicon substrate.

Summary

Thin films of 3C-SiC have been grown in a cold wall CVD reactor at different temperatures and C/Si ratios. A growth series for increasing temperature towards 1200°C shows grain-like structures on top of an underlying SiC layer, which origin is attributed to homogenous nucleation in the gas phase. C/Si ratio variations exhibit differences in the film-structure. The growth rates range between 200 nm/h and 300 nm/h. While an increase in propane flow leading to a higher growth rate, a decrease of silane flow has a less significant effect on the growth rate. XRD analysis indicate, that films grown at T < 1200°C are not yet of single crystalline structure.

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