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Defect morphology and strain of CVD grown 3C–SiC layers: effect of the carbonization process

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The heterostructure formed by cubic silicon carbide/silicon (3C–SiC/Si) is very promising as substrate for cubic III-N growth and for SiC devices. Optimized Si substrate carbonization process before the epitaxial growth of SiC, leads to a higher quality of the layer. In this paper, transmission electron microscopy is used to analyze the defect morphology and strain of SiC layers grown by chemical vapor deposition on two differently carbonized substrates, with tensile and compressive strain state. Misfit dislocations, stacking faults and antiphase domains are observed in this heteroepitaxial system. Irrespective of the substrate used, the epitaxial relationship between Si and SiC is good. However, the grain misorientation of the mosaic structure and the strain of the overgrowth layer depend drastically on the carbonization conditions of the silicon substrate.

1 Introduction

Improved 3C–SiC layers on Si substrates are promising templates for, either, high quality III-N growth or SiC device development. Indeed, assuming 4.357 Å as the lattice constant (a) of 3C–SiC and comparing it with the lattice constants of AlN and GaN reported in the literature [1], the lattice-mismatches are 1.1 and 3.5% respectively. This makes 3C–SiC a very important material to be used as a substrate for growing III-N, instead of Si(001) or GaAs(001) whose lattice mismatches are around 20% [2, 3] with respect to AlN and GaN. This high lattice mismatch relaxes via defects formation, degrading the crystalline quality of the layer. On the other hand, SiC is also suitable for simple and cheap devices such as pressure, gas or temperature sensors working in harsh environments, or even microelectromechanical systems [4].

It has been demonstrated that a proper carbonization step prior to epitaxial growth of 3C–SiC on silicon can lead to a higher quality of the layers [5]. In addition, the temperature at which propane is introduced in the reactor during the carbonization plays a crucial role and affects the quality and the strain state of the subsequent epitaxial layer [6, 7]. In Ref. [8] we have already reported that the microscopic strain of the carbonized silicon varied from a tensile to a compressive state when the propane introduction temperature (T_{intro}) changes from below 1030 °C to 1060 °C.

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In this work we report the defect morphology and the microscopic strain of SiC layers re-grown by chemical vapor deposition on two differently carbonized substrates with tensile and compressive strain state, by means of transmission electron microscopy. Planar view and cross section transmission electron microscopy (TEM) preparation were studied by Selected Area Electron Diffraction (SAED) and High Resolution Transmission Electron Microscopy (HRTEM) modes to quantify the residual microscopic strain evolution vs. the SiC thickness.

2 Experimental techniques

3C–SiC epilayers were grown by atmospheric pressure Chemical Vapor Deposition (CVD) in a vertical cold wall reactor. Silane and propane were used as reactants and H_2 as carrier gas. The standard two-steps process involved 10 min carbonization of the substrate at 1150 °C under propane followed by an epitaxial growth at 1350 °C by adding silane (see Ref. [9] for more details). Two sets of samples were prepared over two different (001) carbonized silicon substrates with T_{intro} below and above the critical value of 1060 °C. For both sets of samples, different SiC thicknesses were epitaxially grown at 1350 °C to investigate the strain change vs. thickness. Samples L1, L2 and L3 had 60 nm, 250 nm and 3 μm thick CVD grown SiC on a low T_{intro} carbonized layer (725 °C) while samples H1 and H2 had around 50 and 250 nm thick SiC on a high T_{intro} (1100 °C) carbonized layer.

Conventional TEM (CTEM) and HRTEM were used to analyze the quality of the interface and the defects appearing in the epilayers. SAED patterns provided information regarding the crystalline quality, the strain as well as the defects of the 3C–SiC grown layer. HRTEM analysis was carried out in a Jeol 2000 EX transmission electron microscope operating at 200 kV whereas SAED patterns and CTEM micrographs were recorded in a Jeol 1200 EX TEM working at 120 kV. Specimens were prepared using mechanical grinding and polishing until 70 μm thickness. After that, a cone-like hole was made on the sample until the thickness in the center of the hole was approximately 5 μm. Finally, ion milling was carried out using Ar^+ ions to bombard the surface of the sample at a 10° tilt and a voltage of 5 kV until electron-transparency.

3 Experimental results and discussion

The Si template used to grow epitaxially the 3C–SiC was, firstly, carbonized with two different T_{intro} which, among other things, dramatically affects the crystalline quality of the carbonized layer. Carbonization at low T_{intro} produces nearly monocrystalline layer consisting of small subgrains with a little misorientation among them. If a high T_{intro} is used to the carbonization process, the subgrains have a higher diameter and a higher misorientation, and the layers are nearly polycrystalline. In order to analyze the crystalline quality of the re-grown layers, SAED patterns were taken in [001] zone axis. Figure 1a and 1b show diffraction patterns of SiC CVD layers over carbonized silicon with low (L1 sample) and high

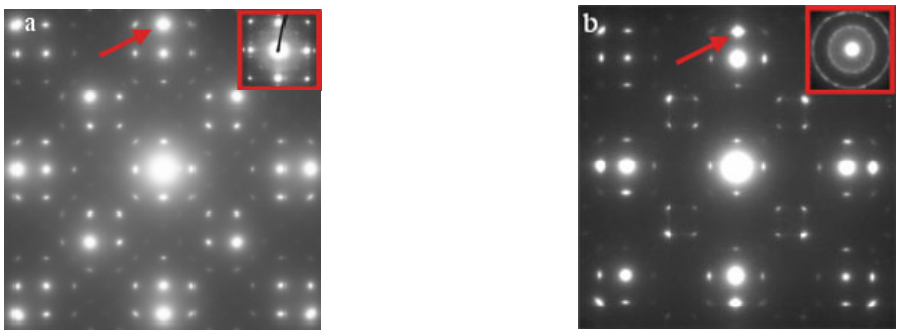

Fig. 1 (online colour at: www.pss-a.com) SAED patterns on [001] zone axis of a) sample E17 and b) E37. The insets show SAED patterns of the carbonized silicon used as substrate in each case.

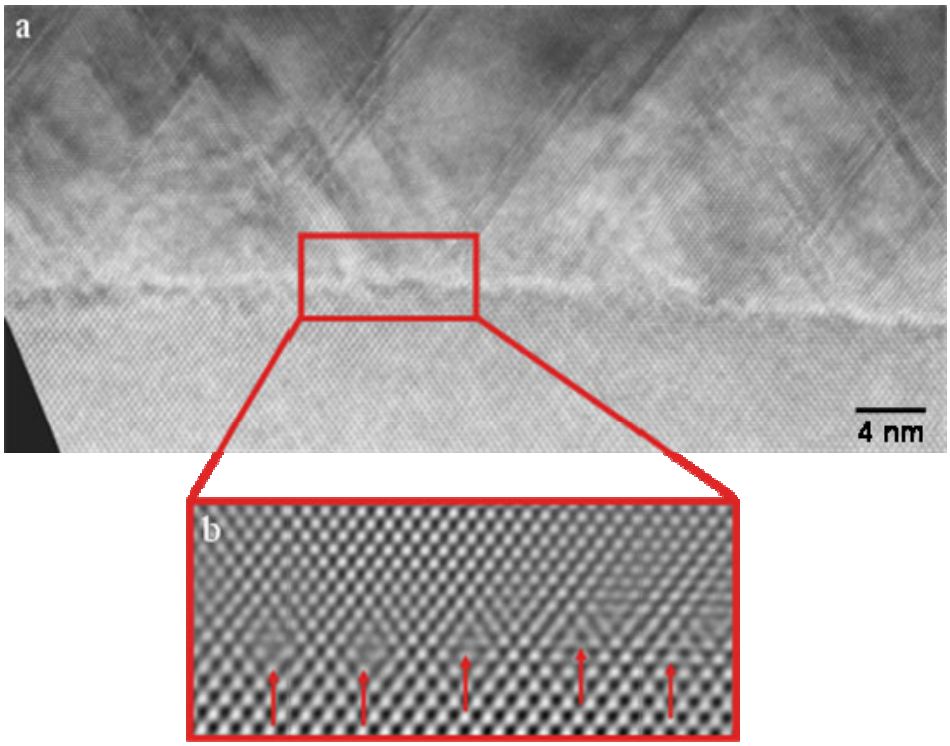

Fig. 2 (online colour at: www.pss-a.com) a) Cross section HRTEM micrograph in ⟨110⟩ zone axis of sample L3 with low T_{intro} (725 °C) carbonization showing the SiC/Si interface and b) filtered image of a part of the interface showing misfit dislocations.

(H1 sample) T_{intro} respectively. The alignment of SiC spots with respect to the Si spots is perfect for both samples what shows the epitaxial character of the growth. However, SiC diffracted spots have curved and elongated shapes, instead of a circular shape, indicating a pseudogranular structure in the SiC with slight variations on their orientation (mosaic structure). If we compare the elongation of the same reflection for two different samples (see arrows in Fig. 1) we can get some qualitative idea about the misorientation. The {400} SiC spots are more elongated in sample H1 than in L1 as a result of the higher misorientation of the underneath carbonized layer (see insets in Fig. 1a and 1b). However, the subgrain misorientation in sample H1 is much lower compared with the carbonized layer over which it has been grown (inset in Fig. 1b). As no evidence for rings appear in its diffraction pattern, a reconstruction or reorganization of the carbonized silicon must occur during the epitaxial re-growth process.

In order to relax the stress produced by the high Si/SiC lattice mismatch (~20%), a high density of misfit dislocations appears along this interface. Figure 2a shows a HRTEM micrograph of the Si/3C–SiC interface along the ⟨110⟩ zone axis. In order to determine the dislocation type, the image of the interface was filtered using a Fast Fourier Transform (FFT), applying a mask to the spots from Si and SiC and obtaining the filtered image by inverse FFT as shown in Fig. 2b. It shows the linear misfit dislocation density (see arrows) that correspond to one dislocation on each four {111} Si planes (and, then, on each five {111} SiC planes). These dislocations are mainly Lömer (90° type) ones as observed in the filtered micrograph, that are much more efficient than 60° type for relaxing the strain produced by the 20% lattice mismatch.

Furthermore, as observed in Fig. 2a, this interface is the origin of a high density of planar defects that propagate in the {111} planes direction with an angle around 55 and 125° with respect to the {001} planes. Figure 3a is a SAED pattern along ⟨110⟩ zone axis of the interface Si/SiC on sample L1. The presence of some streaks connecting the SiC related spots (see arrows on Fig. 3a) indicates that the tilted

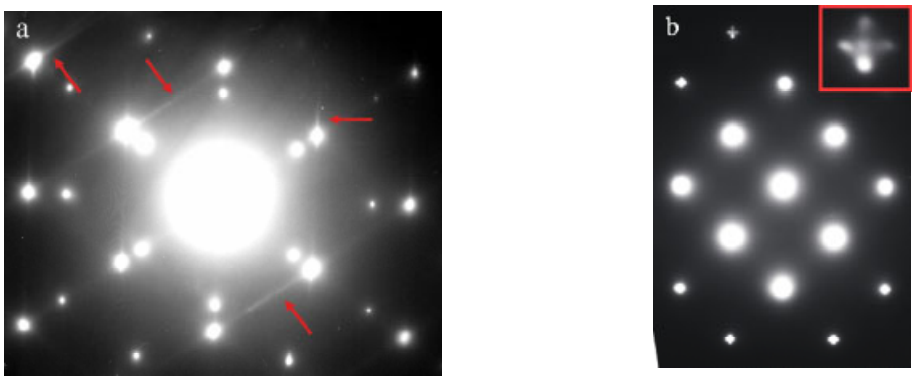

Fig. 3 (online colour at: www.pss-a.com) a) SAED pattern on ⟨110⟩ zone axis of sample L1 showing streaks coming from stacking faults and b) SAED pattern on [001] zone axis of sample L2 revealing the presence of antiphase domains.

contrasts appearing on Fig. 2 can be associated to stacking faults. In addition, the sample with the thickest SiC epilayer grown over the low T_{intro} carbonized silicon, presents antiphase domains. Figure 3b shows a SAED pattern in planar view orientation of that sample in a thin region where only SiC related spots appear. Analysing in detail the lowest intense spots in the image, it can be seen that they consist of a central spot and four more around (see inset). This effect can be associated to the presence of antiphase domains.

SAED patterns as those in Fig. 1 were used to determine the local strain state of the samples. The Si spots were used as a reference to calibrate the image and to calculate the 3C–SiC layer lattice parameter [10]. Using $a_{3C–SiC} = 0.4357$ nm as the lattice parameter of the 3C–SiC, the strain is defined as $S_{3C–SiC} = (a_{3C–SiC\ measured} - 0.4357)/0.4357$, being positive if the microscopic in-plane strain is tensile and negative if it is compressive. The effect of the strain of the carbonized layers used as substrate is analyzed here. The local strain of those carbonized layers, measured using the same method, is +0.5 for the low T_{intro} and –3.5 for the substrate carbonized with $T_{intro} = 1100$ °C. The results of the measurements are summarized in Table 1.

When the carbonized layer presents a tensile strain (due to a low T_{intro} carbonization process) this is conserved during the CVD growth with no variations during the first 5 minutes of growth. This tensile state is the most extensively described in the literature for both the carbonized and epitaxially re-grown layers [11–13]. However, if 3C–SiC is epitaxially re-grown over high T_{intro} carbonized silicon, the microscopic strain state of the layer can change as the re-growth process occurs. After one minute of CVD growth, the lattice parameter of silicon carbide is the same as the nominal value. After five minutes, it has changed to a tensile state and the residual strain is near the +0.3% value measured in the low T_{intro}

Table 1 Summarized results of the strain measured in the different samples.

sample code	sample description	temperature of propane introduction (°C)	SiC thickness (nm)	strain (%)
M769	carbonized Si	725	–	+0.4
L1	carbonized Si + CVD growth	725	60	+0.3
L2	carbonized Si + CVD growth	725	250	+0.3
L3	carbonized Si + CVD growth	725	3000	+0.5
M764	carbonized Si	1100	–	–3.5
H1	carbonized Si + CVD growth	1100	~50	0.0
H2	carbonized Si + CVD growth	1100	~250	+0.2

samples. It seems then that the tensile in-plane strain is the most stable situation for 3C–SiC epitaxially re-grown layer over carbonized silicon and those samples grown over compressive buffer layers prepared under compression, tend to the tensile state as the growth process takes on.

4 Conclusions

In summary, the analysis of 3C–SiC CVD grown over two different carbonized silicon templates has been reported. The crystalline quality of the SiC epilayers is remarkable in all samples, even in those with nearly polycrystalline carbonized silicon as an intermediate buffer layer. Diffraction patterns reveal the presence of both stacking faults and antiphase domains. They show also that the microscopic strain of the SiC epitaxially re-grown is affected by the local strain state of the buffer layer. Samples grown over low T_{intro} carbonized Si vary their strain as the CVD process occurs, changing from compressive to tensile state. Further analyses are in progress in order to understand the mechanism of the strain relaxation during the crystal growth.

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