



**HAL**  
open science

## Ge Mediated Surface Preparation for Twin Free 3C-SiC Nucleation and Growth on Low Off-Axis 4H-SiC Substrate

K. Alassaad, M. Vivona, V. Soulière, B. Doisneau, F. Cauwet, D. Chaussende,  
F. Giannazzo, F. Roccaforte, Gabriel Ferro

► **To cite this version:**

K. Alassaad, M. Vivona, V. Soulière, B. Doisneau, F. Cauwet, et al.. Ge Mediated Surface Preparation for Twin Free 3C-SiC Nucleation and Growth on Low Off-Axis 4H-SiC Substrate. ECS Journal of Solid State Science and Technology, 2014, 3 (8), pp.P285 - P292. 10.1149/2.0121408jss . hal-01615319

**HAL Id: hal-01615319**

**<https://hal.science/hal-01615319>**

Submitted on 16 Oct 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Ge mediated surface preparation for twin free 3C-SiC nucleation**  
2 **and growth on low off-axis 4H-SiC substrate**

3 K. Alassaad<sup>1</sup>, M. Vivona<sup>3</sup>, V. Soulière<sup>1</sup>, B. Doisneau<sup>2</sup>, F. Cauwet<sup>1</sup>, D. Chaussende<sup>2</sup>, F.  
4 Giannazzo<sup>3</sup>, F. Roccaforte<sup>3</sup>, G. Ferro<sup>1\*</sup>

5 <sup>1</sup>Université Claude Bernard Lyon 1, CNRS, UMR 5615, Laboratoire des Multimatériaux et  
6 Interfaces, 43 Bd du 11 Nov. 1918, 69622 Villeurbanne –France

7 <sup>2</sup>Univ. Grenoble Alpes, LMGP, F-38000 Grenoble, France

8 <sup>3</sup>CNR-IMM, Strada VIII, n. 5 – Zona Industriale, 95121 - Catania, Italy

9

10

11

12 Corresponding author \* [gabriel.ferro@univ-lyon1.fr](mailto:gabriel.ferro@univ-lyon1.fr)

Ge mediated surface preparation for 3C-SiC nucleation and growth on low off-axis 4H-SiC  
substrate

1 **Abstract**

2 In this work, we report on the effect of adding GeH<sub>4</sub> during 3C-SiC heteroepitaxial growth on  
3 low off-axis 4H-SiC substrate using chemical vapor deposition technique. When added together  
4 with SiH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>, GeH<sub>4</sub> does not significantly modify the 3C layer quality which contains a  
5 high density of twin boundaries. But when it is introduced before the growth, i.e. during a  
6 surface pretreatment step at 1500 °C, a remarkable change in the layer morphology is seen.  
7 Furthermore for optimal GeH<sub>4</sub> flux, twin boundaries are completely eliminated. Investigation of  
8 the results obtained when varying growth parameters (temperature, C/Si ratio, gas composition  
9 during the surface preparation) allowed proposing a mechanism leading to twin boundary  
10 elimination. It involves a transient homoepitaxial growth step followed by 3C nucleation when  
11 large terraces are formed by step faceting. Preliminary electrical characterizations of the twin  
12 free 3C-SiC layers, using conductive atomic force microscopy (c-AFM), are given.

13

14 **Keywords:** Ge, twin free, 3C nucleation and c-AFM

15

16 **Introduction**

17 The properties of silicon carbide (SiC) make it an appropriate material for high temperature,  
18 harsh environments and high power electronics <sup>1</sup>. In the past years, 4H-SiC based devices have  
19 been mainly developed due to its relative superior properties compared to those of other  
20 polytypes and its commercial availability as large area and high quality seed crystals. The  
21 technology based on 3C-SiC polytype, despite its higher electron mobility and better SiO<sub>2</sub>/SiC  
22 interface <sup>2 3</sup>, is still far behind due to the lack of commercial substrate.

23

1 The most studied solution for growing epitaxial 3C-SiC was (and is still) the use of Si substrate,  
2 with a two-step chemical vapor deposition (CVD) process <sup>4</sup>. However, the high lattice and  
3 thermal expansion mismatches between SiC and Si lead to still unsolved difficulties in terms of  
4 crystalline quality and wafer bowing <sup>5</sup>. Among the various attempts for solving these problems,  
5 the use of Ge pre-deposition was proposed as a way to reduce the stress in the 3C-SiC layer and  
6 improve the crystalline quality <sup>6-8</sup>. Switching to better matched hexagonal SiC substrates is  
7 possible when using on-axis or low off-axis (0001) substrate. Virtually, high quality 3C-SiC  
8 (111) can be grown on it by resolving the stress and mismatch issues but this is not the case  
9 experimentally. Indeed it creates a new difficulty, i.e. the quasi-systematic formation of twin  
10 defects (also called double positioning boundary or DPB).

11  
12 Different techniques were explored for the DPB density reduction in the 3C-SiC grown layers on  
13 commercial  $\alpha$ -SiC substrates. The more frequent attempts were using liquid-based techniques  
14 which seem to be more adapted. For instance, vapor-liquid-solid (VLS) mechanism established  
15 the ability to produce DPB-free 3C-SiC layers but homogeneity, sample size and impurity level  
16 are still pending issues <sup>9</sup>. More recently, Ujihara et al using top seeded solution growth (TSSG)  
17 demonstrated high quality 3C on 6H substrate although a few DPBs and 6H-inclusions remained  
18 <sup>10</sup>. Using high temperature vapor phase process (CFPVT), it was demonstrated the possibility to  
19 grow large area DPB free, thick 3C-SiC layers but reproducibility and control of the process are  
20 very difficult <sup>11</sup>. **There have been other few studies on the heteroepitaxial growth of**  
21 **3C-SiC on 6H-SiC substrates by other non-CVD techniques <sup>12, 13</sup>. They pointed out**  
22 **the possibility of reducing the twins' density by varying different growth**  
23 **conditions.**

1  
2 The use of CVD based approach should be the best solution due its high scalability,  
3 reproducibility and the good performances of the SiC-CVD reactors. But, very few attempts  
4 were successful for DPB elimination using this technique, most probably due to the lack of a full  
5 understanding of the fundamental reasons which can help selecting one of the two possible 3C  
6 orientations. From the literature, it is obvious that the in-situ surface preparation of the substrate  
7 before 3C growth plays a major role in twin density reduction <sup>14-19</sup>. Pure hydrogen or carbon-rich  
8 conditions were studied as surface preparation steps. Addition of chlorine during the growth  
9 seems to improve the process <sup>15,17</sup>. The growth temperature could be as low as 1350°C <sup>15-17</sup> while  
10 other studies suggest better results at higher temperature <sup>20</sup>.

11 An interesting approach was proposed by Neudeck et al., in which 0.2mm×0.2mm mesas were  
12 used to produce step free surfaces and to grow subsequently 3C-SiC layers without DPBs <sup>21</sup>.  
13 However, the local presence of screw dislocations reduces the yield of fabrication of these step  
14 free mesas. As a result, more work is needed to understand and master the nucleation and growth  
15 in this difficult heteroepitaxial system.

16 To the best of our knowledge, the effect of adding a foreign iso-electronic element, such as Ge,  
17 before or during 3C-SiC growth on (hexagonal)  $\alpha$ -SiC substrate-using CVD has not been  
18 reported yet. In the present study, we report the effect of adding GeH<sub>4</sub> to the standard chemistry  
19 H<sub>2</sub>-SiH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> CVD system.

20

## 21 **Experimental Details**

22

1 The experiments were carried out in homemade epitaxy equipment working at atmospheric  
2 pressure. It is composed of a 70 mm diameter vertical cold wall reactor made of quartz and  
3 equipped with a homogenization grid on its upper part. The samples are held on a cylindrical SiC  
4 covered graphite susceptor, 40 mm in diameter, which is inductively heated. The substrate  
5 temperature is monitored with an optical pyrometer connected to a temperature controller. High  
6 purity hydrogen (16 slm), silane (1.25 to 5 sccm) and propane (2.1 to 8.33 sccm) are used,  
7 respectively, as vector gas and precursors for the SiC growth. C/Si ratio was set to 5 except when  
8 mentioned differently. The growth rate was changed from 1.25 to 5  $\mu\text{m}/\text{h}$  and deposition  
9 occurred on  $1 \times 1 \text{ cm}^2$  pieces sawed from complete commercial 4H-SiC wafers nominally on-axis  
10 (0001) Si face unless specified differently. Addition of high purity  $\text{GeH}_4$  gas (0.02 to 0.2 sccm)  
11 was used either during the deposition time or during the in situ surface pre-treatment of the  
12 substrates, i.e. before adding  $\text{SiH}_4$  and  $\text{C}_3\text{H}_8$  to start the CVD growth. These pre-treatments  
13 typically involved introducing  $\text{GeH}_4$  flux in the reactor at  $1500^\circ\text{C}$  for 10 min.

14  
15 The layers were routinely characterized by Nomarski optical microscopy and  $\mu$ -Raman  
16 spectrometry for surface morphology and polytype determination. The HeNe laser beam ( $\lambda = 633$   
17 nm) was focused down to a spot of a few micrometers squared in a confocal mode configuration.  
18 Atomic force microscopy (AFM), composed of a Scientec, picoscan 5 apparatus, was used in the  
19 nucleation study. Complementary information was obtained using electron backscattered  
20 diffraction (EBSD) for surface mapping of the grown polytype, with the possibility of separating  
21 areas with different orientation, such as on each side of a twin boundary<sup>22</sup>. The imaging was  
22 performed using a TSL (TexSEM Lab.) system installed on a ZEISS Ultra 55 FEG SEM with the

1 Orientation Imaging Microscopy TM software. EBSD mappings were made on a large area up to  
2 (250x250  $\mu\text{m}^2$ ) with a very low step ( $\leq 1.5 \mu\text{m}$ ).

3

4 A morphological characterization of the 3C-SiC epilayer was performed by a Veeco DI  
5 dimension 3100 atomic force microscope (AFM), equipped with a nanoscope V electronics. The  
6 two dimensional current distribution was monitored using a conductive module (C-AFM) and  
7 correlated to the epilayer morphology. ~~In order to study the electrical behavior of these samples,~~  
8 ~~circular Schottky contacts of different radii (ranging from 5 to 150  $\mu\text{m}$ ) were fabricated using Au~~  
9 ~~as barrier metal. Due to the typically high defect density in this material, a rectifying behavior~~  
10 ~~has been observed only for the smallest contacts. Hence,~~ **In order to study the electrical behavior**  
11 **of these samples, firstly an Ohmic back-contact based on nickel silicide was fabricated by Ni-**  
12 **deposition followed by a rapid thermal annealing (RTA) treatment at 950°C. Then, circular**  
13 **Schottky contacts of different radii were defined by Au-sputtering, optical lithography and wet**  
14 **etching. Due to the typically high defect density in this material, a rectifying behavior was**  
15 **observed only for the smallest diodes. Thus, diodes with radius of 5 or 10  $\mu\text{m}$  were investigated.**  
16 The biased conductive tip of the AFM has been used in order to acquire the current-voltage (I-V)  
17 characteristics of these small Au-contacts, as reported elsewhere in more detail <sup>23</sup>.

18

### 19 **3C-SiC CVD growth results**

20

21 Our usual in situ surface preparation step before CVD growth involves an etching under  $\text{C}_3\text{H}_8$  for  
22 10 min. When using such procedure, the 3C-SiC layer grown at 1500°C is highly twinned as can  
23 be seen in Figure 1a which displays a dense and random network of DPBs. Similar result is

1 obtained when keeping the same procedure and adding 0.1 sccm GeH<sub>4</sub> during the growth (Figure  
2 1b). One can see that the average density, size and shape of the DPBs are not much affected by  
3 the addition of GeH<sub>4</sub> (in the 0.02 to 0.2 sccm flux range of the present study). Note in this case  
4 that some Ge accumulates on the surface and forms micrometric to nanometric droplets  
5 decorating the DPBs. If now 0.02 sccm of GeH<sub>4</sub> is added together with propane during the in situ  
6 surface preparation, no change in the surface morphology can be noticed. But if the GeH<sub>4</sub> flux  
7 increases to 0.06 sccm or higher (while keeping propane constant), the morphology significantly  
8 evolves (Figure 2). It is still composed mostly of 3C polytype (as seen from  $\mu$ -Raman  
9 spectroscopy) but exhibits elongated features, oriented toward the same directions. This is first  
10 evidence that Ge element can modify the 3C nucleation on low off axis SiC substrate. Finally,  
11 using GeH<sub>4</sub> alone (without C<sub>3</sub>H<sub>8</sub>) during the 10 minutes surface preparation leads to considerable  
12 morphological changes (Figure 3 to 6). The best result was obtained for the case of 0.06 sccm  
13 GeH<sub>4</sub> flux (Figure 3). The layer is globally much smoother and is composed of triangular  
14 hillocks (all oriented toward the same direction) surrounded by large step bunched areas (Figure  
15 3a). Raman spectroscopy evidenced that the layer is of the 3C polytype, even on the triangular  
16 hillocks (Figure 3b). The most surprising and positive result came from EBSD phase mapping  
17 which shows that the layer is not only 100% 3C-SiC, but also it is almost twin free (Figure 3d).  
18 In particular, no twinning could be detected at the places where the triangles are located.

19  
20 When using the minimum GeH<sub>4</sub> flux (0.02 sccm) for surface preparation (Figure 4a), the layer  
21 appears similar to that grown when adding both GeH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> (Figure 2), EBSD phase  
22 mapping showed that the layer is mostly composed of twinned 3C with few hexagonal inclusions  
23 (Figure 4b). When increasing GeH<sub>4</sub> flux to 0.10 sccm, the layer was mainly homoepitaxial with



1 high amount of carrot like 3C inclusions (Figure 5). By further increase of GeH<sub>4</sub> flux to 0.20  
2 sccm during surface preparation, the morphology after CVD growth was rather similar as with  
3 0.10 sccm of GeH<sub>4</sub>, i.e. mainly 4H homoepitaxial layers with triangular 3C inclusions (Figure  
4 6a).

5  
6 For comparison purpose, an experiment was performed using SiH<sub>4</sub> instead of GeH<sub>4</sub> during the  
7 surface preparation, at a flux of 0.06 sccm (identical as for sample shown in Figure 3). In this  
8 case, the layer morphology (Figure 6b) is rather similar to the one obtained using high GeH<sub>4</sub>  
9 flux. Raman spectroscopy (not shown) confirmed that the layer is mostly of 4H polytype.

10

11 C/Si ratio, growth temperature and growth rate are the major parameters either for stabilizing one  
12 polytype over the other or determining the quality of the grown layer. Hence, the influence of  
13 these parameters has been studied by keeping the same preparation step as for the best grown  
14 3C-SiC sample shown in Figure 3 (GeH<sub>4</sub> = 0.06 sccm at 1500°C for 10 min). For growth  
15 temperatures different than 1500°C, the temperature transition step was very short (< 30 sec) and  
16 performed under H<sub>2</sub> only.

17 After growth at 1450°C, the layer looks very similar to the one grown at 1500°C (Figure 7a). The  
18 surface is again decorated by triangular features, which have apparent smaller mean size and  
19 higher density compared to those seen on sample grown at 1500°C. But when the growth  
20 temperature is increased to 1550°C, the layer is mostly 4H-SiC homoepitaxy (as detected by  
21 Raman spectroscopy) with a high density of triangular defects (Figure 7b). This is more or less a  
22 similar morphology as in Figure 6).

23

1 Concerning the effect of the C/Si ratio, an increase of this ratio to 8 (for a growth at 1500°C) did  
2 not induce any morphological difference compared to C/Si of 5 (Figure 3), i.e. with the  
3 formation of small triangular hillocks, suggesting a twin-free 3C-SiC layer. But when the C/Si  
4 ratio was decreased to 3, the morphology changed significantly (Figure 7c) and the layer is found  
5 to be a mixing of polytypes, as detected by  $\mu$ -Raman analyses performed at various areas.

6  
7 The effect of the growth rate was investigated within the range 1.25 – 5  $\mu\text{m/h}$ . The growth time  
8 is kept constant at 1 hour. At high growth rate of 5  $\mu\text{m/h}$  (Figure 8a), the layer is clearly single  
9 domain 3C-SiC like for sample in Figure 3 (grown at 2.5  $\mu\text{m/h}$ ). The main difference is an  
10 overall rougher surface with higher density of triangular hillocks. On the other hand, the use of  
11 low growth rate (1.25  $\mu\text{m/h}$ ) resulted in very smooth morphology without observable triangular  
12 hillocks or step bunching by Nomarski optical microscopy (Figure 8b). Confirmation of the 3C-  
13 SiC polytype was obtained from EBSD investigation which also revealed that the layer is single  
14 domain, Figure 8c.

15  
16 To better understand the role of Ge in the nucleation stage of 3C-SiC, a series of experiments  
17 targeting the early stage of growth was performed. Such study was rather difficult so that 1° off  
18 oriented substrates were used for reducing the scattering of the results thanks to off orientation  
19 control. The first parameter to be checked was the effect of Ge droplets on the surface  
20 morphology/reconstruction of the 4H-SiC seeds. After performing a 10 min surface preparation  
21 under 0.06 sccm  $\text{GeH}_4$ , the sample was cooled down and analyzed. Not surprisingly, spherical  
22 droplets were seen on the surface and identified as pure Ge by  $\mu$ -Raman spectroscopy (not  
23 shown). After chemical etching of these droplets, AFM revealed that the surface does not exhibit

1 any specific ~~surface reconstruction~~ surface morphology feature like macro-step (Figure 11). As a  
2 first conclusion, GeH<sub>4</sub> gas is not modifying the surface of the seed before starting the growth.  
3 The next step is to see what is happening to this surface at the early stage of SiC growth.  
4 Towards this end, three samples were fabricated with similar surface preparations followed by  
5 30, 60 and 90 s growth respectively. On the sample grown with the shortest time, the presence of  
6 Ge droplets was still seen on the surface. AFM characterization on this sample showed that the  
7 surface is now composed of regular parallel steps with some local triangular protrusions (Figure  
8 12a). The measured step height is around 22 nm. EBSD phase mapping on this sample suggests  
9 that the protrusions are made of 3C-SiC (Green) while the surrounding is 4H-SiC (Red) (Figure  
10 12b). Note that this 3C-SiC is predominantly of one orientation (green color). The surface  
11 coverage of 3C-SiC increases after 60 seconds growth while Ge is no more detected on the  
12 surface (Figure 12c). Again, the 3C-SiC is predominantly of one orientation. Finally, an almost  
13 complete 3C layer with nearly one orientation is then observed after 90 seconds of growth  
14 (Figure 12d). The twinned areas (blue inclusions) are very small and isolated one to each other.

15  
16 It was previously shown that high temperature regrowth on top of 3C-SiC VLS seed could lead  
17 to surface smoothening<sup>24</sup>. That is why the twin-free 3C-SiC layer shown in Figure 3 was  
18 subjected to a CVD regrowth at 1600 °C to try eliminating the triangular features. Figure 9  
19 shows the resulting morphology after 8.5 μm thick regrowth at 1600 °C and C/Si of 5. One can  
20 notice that this thickening led to complete elimination of the triangular features. Instead the  
21 regular 60° jagged step bunching was enhanced and homogeneously distributed on the entire  
22 sample. The resulting 11 μm thick layer “re-growth” looks obviously rougher than before  
23 thickening. This is better seen from the AFM images recorded before and after thickening. The

1 morphological analyses obtained by AFM on a scan area of  $50 \times 50 \mu\text{m}^2$  of the two 3C-SiC  
2 epilayers are reported in Figure 10a and Figure 10b. For the as grown layer, the RMS (acquired  
3 excluding the triangular hillocks) was 5.5 nm while it reaches 17.4 nm after the 8.5  $\mu\text{m}$  further  
4 thickening. It is also worth noting that, in the “regrowth” sample, these steps increased their size  
5 and height with respect to the as grown. Besides these morphological features, the “as-grown”  
6 sample shows several surface defects (i.e., the triangular hillocks visible with a bright contrast in  
7 Figure 10a), some hundreds nanometers high and some micrometers in width.

8

9

## 10 **Discussion**

### 11 **The role of Ge in twin boundary elimination**

12 From these results, it is obvious that Ge element can help improving the quality of the 3C-SiC  
13 grown on low off-axis 4H-SiC (0001) substrate. However, its effective role needs to be clarified.  
14 When  $\text{GeH}_4$  is simply added during the growth, DPB density in the grown layer is the same as  
15 without  $\text{GeH}_4$  addition. This later means at least that Ge element does not favor eliminating the  
16 DPBs, for instance by changing their propagation direction like mentioned in ref <sup>25</sup>. Ge atoms  
17 basically accumulate on the surface and incorporate to a certain extent inside the matrix <sup>26</sup>, but  
18 apparently do not affect significantly the growth itself. When considering the positive results  
19 obtained when adding  $\text{GeH}_4$  during surface preparation, one can say that, in order to affect SiC  
20 nucleation, Ge needs to be present on the surface in a certain amount before starting the growth.  
21 Namely, it is not enough to introduce  $\text{GeH}_4$  at the same time as starting SiC growth.

22

1 When GeH<sub>4</sub> is introduced during the surface preparation, the most obvious consequence is its  
2 accumulation on the surface under the form of separated droplets whose size depends on the  
3 GeH<sub>4</sub> flux. The simple presence of Ge droplet on the surface directly affects the 3C-SiC  
4 nucleation. However, in order to eliminate the DPBs from the 3C-SiC grown layer, having Ge  
5 droplets on the surface before growth is not enough. For instance, if propane is added to GeH<sub>4</sub> or  
6 if the GeH<sub>4</sub> flow itself is not adequate during surface preparation, then DPBs are formed or 4H  
7 polytype inclusions can be obtained.

8  
9 Clearly, according to the literature works, the exact mechanism allowing DPB elimination inside  
10 vapor phase grown 3C-SiC on  $\alpha$ -SiC substrate is still under debate <sup>14 15 20 27</sup>. In all the works, the  
11 surface preparation is reported to be a crucial phase and interaction of the nuclei with step edges  
12 is also mentioned. Indeed, our present investigation confirms the importance of this surface  
13 preparation step. The best proof is that the parameter window for surface preparation is very  
14 narrow (only 0.06 sccm GeH<sub>4</sub>, without other gases) while it is much less narrow for the growth  
15 itself (temperature from 1450 and 1500 °C, C/Si ratio from 5 to 8 and growth rate between 1.25  
16 to 5  $\mu\text{m/h}$ ).

17  
18 ~~From this set of samples~~ from the results of the nucleation study, we propose the following  
19 mechanism which is summarized in Figure 13. The first conclusion which can be made is that  
20 growth does not start directly with 3C-SiC but with a transient 4H-SiC homoepitaxial period  
21 (Figure 12ab). This delay in 3C-SiC growth is attributed to the presence of Ge atoms on the  
22 surface. Indeed, as seen from Figure 5, a high flux of GeH<sub>4</sub> during surface preparation promotes  
23 the stabilization of 4H homoepitaxy against 3C nucleation despite the low off-axis of the seeds.

1 In order to interpret this result different scenarii can be proposed. Ge atoms can induce an  
2 enhancement of the surface mobility of Si and C adatoms so that they can more easily reach the  
3 step edges. Another possibility is that Ge can reduce (or even remove) the 3C nucleation sites or  
4 can lower the probability of 2D nucleation on terraces. Note that these two proposed effects of  
5 Ge atoms do not take into account the fact that these Ge atoms are agglomerated under the form  
6 of droplets. We believe that the main effect of these droplets is to act as many local sources of  
7 gaseous Ge by their progressive evaporation.

8

9 After the initial homoepitaxial growth, the step front **should** start to become irregular with the  
10 local formation of ~~perfectly~~ on-axis facets (Figure 12b). These facets ~~are obviously~~ should be  
11 preferential sites for 3C nucleation (Figure 12**ab**). Then the 3C coverage increases either by  
12 lateral expansion of the initial nuclei or by the formation of new on-axis facets and 3C nucleation  
13 on them, until an almost complete 3C coverage is reached (**Figure 12d**) ~~after ~90 sec of growth~~.  
14 Note that the preferential selection of one orientation of the deposited 3C (which should lead to  
15 DPB free layer) seems to occur from the beginning. The lateral expansion of the 3C nuclei favors  
16 selecting at the end one among the two possible orientations. Such mechanism is very similar to  
17 the one proposed by Latu-Romain et al <sup>27</sup>. **It is important to emphasize that within this scenario**  
18 **Ge atoms are just directly affecting the homoepitaxial growth and the faceting. The 3C-SiC**  
19 **nucleation is only the consequence of the faceting.**

20 Another important conclusion from this nucleation study is that, to avoid twin formation, one has  
21 to finely control the 3C nucleation. In the present study, this is a self-controlled process mediated  
22 by the presence of Ge on the surface. Ge should play the role of transient 4H homoepitaxy  
23 promoter so that SiC growth does not start with 3C-SiC. The transition from 4H to 3C occurs

1 smoothly, at separated places where on-axis facets form, which should leave the time for the  
2 early nucleated 3C islands to expand laterally. Though the exact reason for orientation selection  
3 is still to be found, we believe that the key parameter is to be able to move progressively from  
4 homo to heteroepitaxy, in the same way as in reference <sup>27</sup>. Note that the “selection rule”  
5 (inheritance of 3C orientation from the terraces) as described in ref<sup>21</sup> could be considered also for  
6 promoting orientation selection. Using this model, 4H-SiC substrate is found better for  
7 eliminating DPBs but SFs can be formed above step edges so that it might explain the stacking  
8 faults presence inside the layer (as discussed below).

9  
10 All the twin free layers obtained in this study display triangular hillocks on the surface, which do  
11 not correspond to inclusions of polytype or to twinned 3C areas. We believe that this could be  
12 the result of some overgrowth of these early formed inclusions. After thickening of a twin free  
13 layer (Figure 9), all the triangular hillocks have vanished, which means that they are just  
14 transient morphological features. This result goes well with the hypothesis of early inclusion  
15 overgrowth which should happen only once and at the beginning. But the negative point brought  
16 to light by the regrowth experiment is that increasing 3C thickness also leads to surface  
17 roughening by enhanced step bunching. This may be the consequence of the growth on low off-  
18 angle which is known to favor step bunching <sup>28</sup>.

19  
20 Some of the samples grown in this study display both 4H and 3C areas which suggest a  
21 competition between homo and heteroepitaxy all along the growth runs. This is layers grown  
22 with high GeH<sub>4</sub> fluxes, low C/Si ratios, high temperatures and excess of Si on the surface before  
23 growth. High temperatures and low C/Si ratios are known parameter promoting homoepitaxy <sup>20</sup>.

1 Having excess of Si on the surface before growth is similar to having a low C/Si ratio at the  
2 beginning of the growth. And as discussed earlier, excess of Ge atoms on the surface seems to  
3 promote homoepitaxy. As a consequence, using conditions promoting 4H homoepitaxy is not  
4 good for twin boundary elimination. It probably delays too much the transition from 4H to 3C so  
5 that the 3C nucleation is too scarce. It then remains as isolated islands and leads to the formation  
6 of 3C inclusions in a hexagonal layer.

7

### 8 **Electrical characterization results**

9 A preliminary electrical characterization was carried out to get insight on the quality of the  
10 obtained twin free 3C layer and monitor the presence of electrically active defects on the surface.  
11 The measurements were conducted on an “as-grown” layer shown in Fig. 3 and on the  
12 “regrowth” sample presented in Figure 9. The electrical behavior of the epilayer surface was  
13 investigated at nanometric scale by means of C-AFM and correlated with the surface  
14 morphology. The AFM surface morphology images are reported in Figures 14a and 14b, while  
15 the corresponding C-AFM current maps are reported in Figures 14c and 14d. As can be seen, the  
16 nanoscale electrical behaviour of the two samples was rather similar. In particular, in the two  
17 dimensional current maps of the “as-grown” (Figure 14c) and the “re-growth” (Figure 14d), two  
18 types of electrically active features are observed. Firstly, some conductive structures resembling  
19 the surface steps and observed in the morphological analysis are clearly visible also in the C-  
20 AFM, especially for the “as grown” sample (Figure 14c). This observation can be attributed to an  
21 enhanced conduction in the sidewalls of the surface steps, due to the increased contact area of the  
22 probe tip encountering such morphological features. In addition, most interesting is the presence  
23 of some isolated electrically active defects lines, forming an angle of  $\sim 55^\circ$  with respect to the



1 morphological surface steps, which are visible in the two samples. Some of these defects were  
2 marked by red lines in Figures 14c and 14d. These electrically active defects can be ascribed to  
3 electrical signatures of stacking faults (SFs).

4 From the two dimensional current maps, it was possible to estimate a density of the electrically  
5 active defects in the order of the mid  $10^2 \text{ cm}^{-1}$  range, in both cases. Hence, the different surface  
6 roughness, 5.5 nm for the “as-grown” (Figure 14a) and of 17.4 nm for the “re-growth” (Figure  
7 14b) samples, seems to be not directly correlated to the density of these defects.

8 The electrical investigation of the Au-contacts on both epilayers was carried out by C-AFM on  
9 the small devices, i.e. those showing a rectifying behavior. **Figure 15 reports the J-V**  
10 **characteristics for the as-grown and re-grown samples. Both contacts behave as Schottky diodes**  
11 **with low barrier height. Quantitatively, comparable values of the barrier height were found in the**  
12 **as-grown sample (0.76 eV) and in the re-grown case (0.73 eV). The derived Schottky barrier**  
13 **heights result lower than the ideal value of  $\sim 1.3 \text{ eV}$ , predicted by the Schottky-Mott theory and**  
14 **given from the difference between the metal work function and the semiconductor electron**  
15 **affinity. The deviation of the Schottky barrier height from the ideal behavior can be ascribed to**  
16 **the presence of electrically active defects in the 3C material, which provide preferential current**  
17 **paths through the epilayer, as already reported in ref. <sup>23</sup>. The two diodes exhibit high ideality**  
18 **factor values (3.3 and 1.8 for the as-grown and regrown layers, respectively), consistently with a**  
19 **non-perfect Schottky behavior and a strong recombination of the direct current. Regarding the**  
20 **reverse behavior with the characteristics reported in the inset of Figure 15, the two samples**  
21 **show leakage currents of the same order of magnitude ( $1 \times 10^{-7} \text{ A/cm}^2$ ), with a slight lower value**  
22 **in the case of the as-grown layer, in agreement with the higher value of Schottky barrier height.**

23

## 1 **Conclusion**

2 Pre-treatment under GeH<sub>4</sub> of low off-axis 4H-SiC seeds was found to positively affect the 3C-  
3 SiC nucleation up to the complete elimination of twin boundaries under optimal conditions. The  
4 proposed mechanism involved a smooth transition between 4H homo and 3C heteroepitaxy  
5 thanks to the presence of Ge on the surface which transiently promotes 4H homoepitaxy. Based  
6 on a similar mechanism than the one proposed in ref 22, which was described but not really  
7 controlled, here we demonstrate that the transition can be effectively controlled in a CVD reactor  
8 if it is mediated by Ge atoms. This result could pave the way of a future development of large  
9 size and high quality 3C-SiC epilayers. A preliminary electrical characterization confirms the  
10 good quality of the grown layers.

## 11 **Acknowledgements**

12 This work is financially supported by Marie Curie Actions under the project n°264613-NetFISiC

## 13 **References**

- 14 1. S. E. Saddow and A. K. Agarwal, *Advances in Silicon Carbide Processing and*  
15 *Applications* (Artech House, Inc, Norwood, MA, 2004).
- 16 2. A. Schöner, M. Krieger, G. Pensl, M. Abe, and H. Nagasawa, *Chem. Vap. Deposition* **12**,  
17 523 (2006).
- 18 3. J. Lorenzzi, R. Esteve, N. Jegenyés, S. A. Reshanov, A. Schöner, and G. Ferro, *J.*  
19 *Electrochem. Soc.* **158**, 630 (2011).
- 20 4. S. Nishino, J. A. Powell, and H. A. Will, *Appl. Phys. Lett.* **42** 460 (1983).
- 21 5. A. Severino, et al., *ECS Trans.* **35**, 99 (2011).
- 22 6. P. Masri, N. Moreaud, M. R. Laridjani, J. Calas, M. Averous, G. Chaix, A. Dollet, R.  
23 Berjoan, and C. Dupuy, *Mater. Sci. Eng. B* **61-62**, 535 (1999).

- 1 7. J. Pezoldt, C. Förster, P. Weih, and P. Masri, *Appl. Surf. Sci.* **184**, 79 (2001).
- 2 8. C. Zgheib, L. E. McNeil, P. Masri, C. Förster, F. M. Morales, T. Stauden, O. Ambacher,  
3 and J. Pezoldt, *Appl. Phys. Lett.* **88**, 211909 (2006).
- 4 9. M. Soueidan and G. Ferro, *Adv. Funct. Mater.* **16**, 975 (2006).
- 5 10. T. Ujihara, R. Maekawa, R. Tanaka, K. Sasaki, K. Kuroda, and Y. Takeda, *J. Cryst.*  
6 *Growth* **310**, 1438 (2008).
- 7 11. D. Chaussende, L. Latu-Romain, L. Auvray, M. Ucar, M. Pons, and R. Madar, *Mater.*  
8 *Sci. Forum* **483-485**, 225 (2005).
- 9 12.
- 10 13.
- 11 14. Z. Y. Xie, J. H. Edgar, B. K. Burkland, J. T. George, and J. Chaudhuri, *J. Cryst. Growth*  
12 **224**, 235 (2001).
- 13 15. A. Henry, S. Leone, F. C. Beyer, S. Andersson, O. Kordina, and E. Janzén, *Mater. Sci.*  
14 *Forum* **679-680**, 75 (2011).
- 15 16. X. Li, H. Jacobson, A. Boulle, D. Chaussende, and A. Henry, *ECS Journal of Solid State*  
16 *Science and Technology* **3**, P75 (2014).
- 17 17. S. Leone, F. C. Beyer, A. Henry, O. Kordina, and E. Janzén, *Phys. Status Solidi RRL* **4**,  
18 305 (2010).
- 19 18.
- 20 19.
- 21 20. M. Soueidan, G. Ferro, B. Nsouli, F. Cauwet, J. Dazord, G. Younes, and Y. Monteil,  
22 *Mater. Sci. Eng., B* **130**, 66 (2006).
- 23 21.

- 1 **22.** D. Chaussende, P. Chaudouet, L. Auvray, M. Pons, and R. Madar, Mater Sci Forum **457-**  
2 **460**, 387 (2004).
- 3 **23.** J. Eriksson, M. H. Weng, F. Roccaforte, F. Giannazzo, S. Leone, and V. Raineri, Appl.  
4 Phys. Lett. **95**, 081907 (2009).
- 5 **24.** N. Jegenyés, J. Lorenzzi, V. Soulière, J. Dazord, F. Cauwet, and G. Ferro, Mater. Sci.  
6 Forum **645-648**, 127 (2010).
- 7 **25.** G. Ferro, edited by F. L. Via (Research Signpost, 2012), Vol. ISBN: 978-81-308-0500-9,  
8 p. 213.
- 9 26. K. ALASSAAD, V. Soulière, F. Cauwet, H. Peyre, D. Carole, P. Kwasnicki, S.  
10 Juillaguet, T. Kups, J. Pezoldt, G. Ferro, Acta Materialia, **in press** (2014).
- 11 27. L. Latu-Romain, D. Chaussende, and M. Pons, Cryst Growth Des **6**, 2788 (2006).
- 12 28. B. Kallinger, P. Berwian, J. Friedrich, and B. Thomas, J. Cryst. Growth **381** 127 (2013).

13

14

## 15 **Legends**

16 **Figure 1.** Surface morphology of 3C-SiC grown layers using pretreatment of 10 min at 1500°C  
17 under 2.5 sccm C<sub>3</sub>H<sub>8</sub>: a) without GeH<sub>4</sub> addition and b) with 0.1 sccm GeH<sub>4</sub> addition during the  
18 deposition time.

19 **Figure 2.** Surface morphology of a layer grown at 1500°C using a surface preparation under 0.06  
20 sccm of GeH<sub>4</sub> together with 2.5 sccm of C<sub>3</sub>H<sub>8</sub>.

21 **Figure 3.** Characterization of a 3C-SiC layer grown after surface preparation of 10 min under  
22 0.06 sccm GeH<sub>4</sub> : a) Surface morphology as observed by optical microscopy, b)  $\mu$ -Raman  
23 spectrum recorded on a triangular hillock, c) and d) respectively SEM image and EBSD phase  
24 mapping of the same area; In d), with blue code meaning that the area has only one 3C

1 orientation denoted as 3C(II) and the white spots corresponds to areas which could not be  
2 indexed by the software due to local surface roughness.

3 **Figure 4.** Characterization of a SiC layer grown after surface preparation of 10 min under 0.02  
4 sccm GeH<sub>4</sub> : a) Surface morphology as observed by optical microscopy, b) EBSD phase  
5 mapping; In b), the colour code is green = 3C(I), blue = 3C(II), red = 4H, white = areas which  
6 could not be indexed by the software due to local surface roughness.

7 **Figure 5.** Characterization of a SiC layer grown after surface preparation of 10 min under 0.1  
8 sccm GeH<sub>4</sub> : a) Surface morphology as observed by optical microscopy, b) EBSD phase  
9 mapping; In b), the colour code is green = 3C(I), blue = 3C(II), red = 4H, white = areas which  
10 could not be indexed by the software due to local surface roughness.

11 **Figure 6.** Surface morphology of epitaxial layers grown after a surface preparation step  
12 performed at 1500°C for 10 min under a) 0.20 sccm of GeH<sub>4</sub> and b) 0.06 sccm of SiH<sub>4</sub>.

13 **Figure 7.** Surface morphology of epitaxial layers grown after the optimal surface preparation  
14 step (1500°C for 10 min under 0.06 sccm of GeH<sub>4</sub>): a) growth temperature of 1450°C and C/Si  
15 of 5, b) growth temperature of 1550°C and C/Si of 5 and c) growth temperature of 1500°C and  
16 C/Si of 3.

17 **Figure 8.** Surface morphology of epitaxial layers grown after the optimal surface preparation  
18 step (1500°C for 10 min under 0.06 sccm of GeH<sub>4</sub>) : a) growth rate of 5 μm/h, C/Si ratio of 5, b)  
19 growth rate of 1.25 μm/h, C/Si ratio of 5; in c) is shown the EBSD phase mapping of sample  
20 displayed in b), with Green code meaning that the area has only one 3C orientation denoted as  
21 3C(I) and the white spots corresponds to areas which could not be indexed by the image software

22 **Figure 9.** Optical image of layer shown in fig. 3 after 8.5 μm thickening at 1600 °C with a C/Si  
23 ratio of 5.

1 **Figure 10.**  $50 \times 50 \mu\text{m}^2$  AFM images of a) the as-grown layer shown in fig. 3a and b) the  
2 regrowth sample in Fig. 9.

3 **Figure 11.** AFM image ( $1 \times 1 \mu\text{m}$  scan) showing the surface morphology of a sample treated 10  
4 min at  $1500^\circ\text{C}$  under 0,06 sccm  $\text{GeH}_4$ , after wet etching of the accumulated Ge droplets on the  
5 surface

6 **Figure 12.** Figure 12. AFM and EBSD characterization of the 3C-SiC nucleation experiments  
7 performed for 30, 60 and 90 seconds at  $1500^\circ\text{C}$  after optimal  $\text{GeH}_4$  surface preparation for  
8 obtaining 3C twin free layer. a)  $95 \times 95 \mu\text{m}^2$  AFM image of the 30 seconds growth experiment  
9 and b) is its equivalent EBSD imaging. c) and d) are the EBSD mapping of the 60 and 90  
10 seconds experiment respectively. The color code is green = 3C(I), blue = 3C(II), red = 4H, white  
11 = areas which could not be indexed by the software due to local surface roughness.

12 **Figure 13.** Mechanism of Ge assisted 3C nucleation on 4H-SiC low off axis seed. (a), 4H-SiC  
13 substrate with  $\text{GeH}_4$  surface preparation, (b), starting the growth by 4H-homoepitaxy along with  
14 the formation of on-axis facets, and (c), nucleation of a 3C-SiC island on the facet and  
15 expansion toward all directions.

16 **Figure 14.** Surface morphologies (a and b) and current maps (c and d) measured by C-AFM on  
17 the “as grown” 3C-SiC sample and “re-growth” one. Electrically conductive defects, most  
18 probably associated to the presence of SFs, are visible in the current map (highlighted by  
19 transversal red lines).

20 **Figure 15.** Forward J-V curves, acquired by C-AFM, related to the “as-grown” layer and “re-  
21 growth” one. The inset reported a semi-log plot of the forward characteristics.