### ELECTRONIC SUPPLEMENTARY INFORMATION

# Nanostructured 3C-SiC on Si by a network of (111) platelets: a fully textured film generated by intrinsic growth anisotropy

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### Additional samples at different temperature and C/Si ratio

To test the robustness of the dendritic growth mode against growth parameters, additional samples have been grown on Si (001) and Si (111), at different temperature and C/Si ratio. More precisely, changing one parameter at a time, we deposited at 1300°C with C/Si ratio 2.2, and at 1250 °C with C/Si ratio 2.6. These conditions still ensure a diffusion-limited regime while allowing for epitaxial growth. A comparison of SEM top views for samples grown on both (001) and (111) substrates is reported in the Fig. S1. In all cases, a texturized film with platelets bounded by {111} side facets is achieved, with orientations reflecting the symmetry of the underlying substrate. Notably, by incrementing the growth temperature from 1250°C to 1300°C, at fixed C/Si=2.6 ratio (see (e) vs. (c) and (f) vs. (d)), the density of platelets is slightly reduced, consistently with an enhancement of surface diffusion. On the contrary, the increment of C/Si ratio from 2.2 to 2.5, at the original growth temperature (see (a) vs. (c) and (b) vs. (d)), does not return any difference, suggesting a minor role of small variations in C/Si ratio once C-rich conditions (C/Si > 2) are established.

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**-**5 μm

**Fig S1** Comparison of SEM top views of 3C-SiC deposition on Si pillars at different growth temperature and C/Si ratio, on both (001) and (111) substrates. Deposition thickness: (a,b) 5  $\mu$ m; (c,d) 7  $\mu$ m; (e) 3.5  $\mu$ m; (f) 4.5  $\mu$ m.

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#### **Molecular Dynamics model and calculation**

We investigated the bulk contribution to the formation energy of the platelets, both if including or not SF bunches, by comparing the layer-by-layer variation of the total energy for one sufficiently large 3D ridge on (001) and (111) and that one for a growing (decorated) triple SFs, as shown in Fig. S2.

Classical molecular dynamics simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).<sup>1</sup> The atomic trajectories were analyzed using the Open Visualization Tool (OVITO) software.<sup>2</sup> The potential energy of the atomic configurations was computed using the Erhart-Albe Analitical Bond-Order interatomic Potential for 3C-SiC (ABOP).<sup>3</sup> ABOP potential has some advantages over other empirical potentials for silicon carbide:<sup>4</sup> it provides an excellent description of the elastic, thermal, and point defect properties of Silicon, Carbon and Silicon Carbide. Although ABOP has first-neighbors-limited interactions, and hence it prescribes zero SF formation energy, it has the advantage with respect to other long-range-interaction potentials for SiC, such as the Vashishta potential,<sup>5</sup> that it correctly allows for the formation of Si-Si and C-C bonds at the 3C-SiC surface. Therefore, it provides a description of the surface energies and reconstructions qualitatively more realistic.

We studied the 3C-SiC (001) and (111) surfaces terminated by Si and C monolayers creating four simulation cells using the following procedure. Orthogonal simulation cells, oriented along the directions determined by the vectors  $u = [1\bar{1}0]$ , v =[110], and w = [100] in the case of the SiC (001) surface and  $u = [1\bar{1}\bar{2}]$ , v = [110], and  $w = [1\bar{1}1]$  in the SiC (111) one. Periodic boundary conditions have been applied along the uand v directions. The two cells encompass from 1024 (no overgrown layers) and 1404 atoms (7 overgrown layers), and their sizes are  $L_x \times L_y \times L_z = 15 \cdot \frac{\sqrt{2}}{2} a \cdot \hat{u} \times 4 \cdot \frac{\sqrt{2}}{2} a \cdot \hat{v} \times 5 \cdot$  $a \cdot \hat{w} = 46.2 \times 12.3 \times 21.7$  Å and  $L_x \times L_y \times L_z = 8 \cdot \frac{\sqrt{6}}{6} a \cdot$  $\hat{u} \times 4 \cdot \frac{\sqrt{2}}{2} a \cdot \hat{v} \times 3 \frac{\sqrt{3}}{3} \cdot a \cdot \hat{w} = 42.7 \times 12.3 \times 22.6$  Å.

To obtain an emerging SF, we displaced the atoms of three consecutive (111) double planes of atoms in each one of the two configurations. Hence, in each cell, the SFs are composed of three consecutive faulted planes. Three consecutive SFs are the simplest way to avoid internal stress in the simulation cell because the correct ordering of (111) planes is preserved at the cell boundaries.

The free (001) surfaces were reconstructed accounting for the  $2 \times 1$  dimer reconstruction.

A minimization procedure was applied for all the presented simulations. It consisted of an initial energy minimization via a conjugated gradient algorithm followed by annealing at 1500 K, followed in its turn by a final minimization.

The simulations were performed in the canonical (NVT) ensemble, using a Nosé–Hoover thermostat.<sup>6</sup> The bottom three layers in the simulation cell were fixed at the atomic position of the bulk to model the effect of the Si substrate



**Fig S2** The atomistic models of a 3D ridge growing on (001) are shown in (a-c) while on (111) in (g-i). The growing triple SF on (001) is shown in (d-f), while on (111) in (j-l). From left to right, we show the flat surface, 3 layers and 7 layers grown on the SiC surface, but not the intermediate configurations.



**Fig S3** The cohesive energy of the different layers for a ridge or a (decorated) SF grown on (001) or (111) is plotted in (a) and (b), respectively.

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below the 3C-SiC layer. The thermal annealing was operated to explore local minima near the initially found minimum for each simulation. It was performed by setting a temperature ramp during the simulation: the system is initially heated from 5 K up to 1500 K in 20 ps, thereafter it is equilibrated at 1500 K for 30 ps, eventually, the system is cooled down to 0.1 K in 50 ps.

This procedure is repeated for the flat surfaces with an emerging SF (Fig. S2a, d, g and j), and for each layer forming a ridge or a SF on the (001) and (111), up to 7 atomic layers, as shown in Fig. S2.

The energy difference (per atom) between the considered cells is plotted in Fig. S3 for the C terminated (001) and Si terminated (111) cases and corresponding to the atomistic models shown in Fig. S2. Except for the very first layers of SF, when the overgrown layers are essentially filling the hole generated by the emerging SF on the surface, thus reducing the surface energy, in all the other cases the cohesive energy is almost constant with the number of overgrown layers and equal for the ridge and SF cases.

## Structural analysis of the platelets symmetry and role of twinning

As discussed in the main manuscript, the 3C-SiC platelets are bounded by two parallel {111} faces, including several SF

planes, parallel to each other and the two faces. It is because of the emergence of such SFs that the side and top facets of the platelets are fast growth fronts. On the contrary, the wide {111} are not intercepted by the SFs and hence have negligible growth at the experimental conditions here returning the dendritic growth mode. Platelets are expected to start growing from on top of the pristine 3D islands, as observed in Fig. 1(a,b) of main manuscript. Then, the vertical and lateral drag provided by the enhanced growth at the emerging SFs, combined with the continuum supply of material from the external flux of C and Si precursors, result in a progressive enlargement of the sheets, starting from a few hundred nms up to microns, as recognizable from the evolution series of Fig. 1(c), 1(e) and 2(c) of the main text. As indicated by the perspective in the SEM views, the upper side of the platelets is larger than its bottom.

Apart of the irregularity along the growth fronts, each platelet can be sketched as an irregular trapezoid aligned as the {111} planes of the generating SFs. Then, the observed orientation of platelets on both (111) and (001)-oriented substrates must reflect the symmetry of the slanted {111} planes emerging it. By considering a top view of the substrate, such {111} planes would correspond to lines along the <110> directions on both substrate orientations.

In Fig. S4 and S5 we analyse the symmetry of the platelets for the (111) and (001) substrate respectively, including the



**Fig. S4** Symmetry and atomic model of the 3C-SiC platelets on Si(111) substrate. Platelets are sketched for both the nominal crystal orientation (coloured in grey) and when including a twin boundary in the {111} basal plane (green).



**Fig. S5** Symmetry and atomic model of the 3C-SiC platelets on Si(001) substrate. Platelets are sketched for both the nominal crystal orientation (coloured in grey) and when including a twin boundary in one {111} plane (green).

possibility of local twinning. In the atomistic reconstructions, we consider a simplified representation of the platelet edges by averaging their irregular profile as {111} planes where SFs (not shown) emerge as in Fig. 6(c).

In the case of a (111) substrate (Fig. S4), the symmetry of the <110> directions is 3-fold and hence only three platelet orientations are expected for the ideal crystal, as illustrated by the grey structures in Fig. S4. However, it is sufficient to admit that twinning occurs in the basal plane of the pristine 3D grains from which the platelets develop to obtain the reversal of the orientation of the SF planes. As shown by the green structures in Fig. S4, this twinning still preserves the alignment of the <110> directions but inverts the inclination of the {111} planes thus doubling the symmetry of the platelets in agreement with the SEM observations (see Fig. 3(g) in main text).

In the case of a (001) substrate (Fig. S5), the symmetry of the <110> directions is 4-fold and hence four platelet orientations are expected for the ideal crystal, as illustrated by the grey structures in Fig. S5. Then, it is again possible to obtain

additional, secondary platelet orientations by repeating the procedure of twinning discussed for the (111) substrate. However, in this case, the {111} twinning planes are not parallel to the surface so that in the twinned region the crystal axis will be rotated. The resulting shape of the platelets, matching the {111} SF planes in the twinned region, according to our atomistic model, is still trapezoidal but the top termination will not be horizontal. In particular, in a top view, the twinned-<110> directions tracing the rim of the platelet will be oriented at a ±30° angle rotation with respect to the <110>-directions in the untwined region, as made evident by the green structures in Fig. S4. By considering the 4-fold symmetry of the (001) substrate, each returning two distinguishable twinning at ±30°, we obtain a total of twelve different platelet orientations in substantial agreement with the experimental observations (see Fig. 1(c-f) and 2(a,c) ). Notably, platelets on twinned patches of the (001) substrate should be more vertical than other platelets. This appears to be indeed the case in many platelets at 30° and 60° in Fig. 2(c), further supporting our interpretation.

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The symmetries in Figs. S4 and S5 are supported by the XRD measurements shown in Fig. S6. For these measurements the diffractometer was aligned on the SiC(224) peak in the asymmetric grazing-incidence geometry, and the scan was performed by rotating the substrate. On (111), peaks at  $\pm 120^{\circ}$  would be expected but peaks at  $\pm 60^{\circ}$  and  $180^{\circ}$  are also seen, consistent with the symmetry Fig. S4. On (001), peaks are seen with a periodicity of  $30^{\circ}$  instead of  $90^{\circ}$  in samples featuring platelets, as described in Fig. S5.

#### References

- 1 S. Plimpton, J. Comput. Phys. 1995, 117, 1.
- 2 A. Stukowski, *Modelling Simul. Mater. Sci.* Eng. **2009**, *18*, 015012.
- 3 P. Erhart, K. Albe, Phys. Rev. B 2005, 71, 035211.
- 4 A. Sarikov, A. Marzegalli, L. Barbisan, E. Scalise, F. Montalenti, L. Miglio, *Modelling Simul. Mater. Sci. Eng.* **2019**, *28*, 015002.
- 5 P. Vashishta, R. K. Kalia, A. Nakano, J. P. Rino, *J. Appl. Phys.* **2007**, *101*, 103515.
- 6 W. Shinoda, M. Shiga, M. Mikami, *Phys. Rev. B* **2004**, *69*, 134103.

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**Fig. S6** Diffracted intensity for the SiC(224) reflection, in the asymmetric grazing-incidence geometry, as a function of substrate rotation angle  $\varphi$  relative to the [110] direction on (001) or the [112] direction on (111). The samples in (a) and (b) correspond to those in Fig. 5(a) and (b) of the main text.