

# 1 RPCVD growth of isolated Ge crystals and 2 suspended layers on micrometric Si pillars

3 *Oliver Skibitzki<sup>1,\*</sup>, Giovanni Capellini<sup>1,2</sup>, Yuji Yamamoto<sup>1</sup>, Peter Zaumseil<sup>1</sup>, Markus Andreas*  
4 *Schubert<sup>1</sup>, Thomas Schroeder<sup>1,6</sup>, Andrea Ballabio<sup>3</sup>, Roberto Bergamaschini<sup>4,\*\*</sup>, Marco*  
5 *Salvalaglio<sup>4,5</sup>, Leo Miglio<sup>4</sup>, Francesco Montalenti<sup>4</sup>*

6 1 IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany

7 2 Department of Science, Università Roma Tre, viale G. Marconi 446, Roma I-00146, Italy

8 3 L-NESS and Department of Physics, Politecnico di Milano, via Anzani 42, I-22100 Como,  
9 Italy

10 4 L-NESS and Department of Materials Science, Università di Milano-Bicocca, Via Cozzi 55, I-  
11 20125, Milano, Italy

12 5 Present address: Institut für Wissenschaftliches Rechnen, Technische Universität Dresden,  
13 Zellescher Weg 12-14, D-01069 Dresden, Germany

14 6 Brandenburgische Technische Universität, Konrad-Zuse-Str. 1, 03046 Cottbus, Germany

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16 KEYWORDS

1 *Virtual substrate, Germanium, Patterned Si, Selective Growth, Vertical heteroepitaxy, Growth*  
2 *dynamics simulation, Dislocations, Reduced pressure chemical vapor deposition.*

3 ABSTRACT

4 In this work, we demonstrate the growth of Ge crystals and suspended continuous layers on  
5 Si(001) substrates deeply patterned in high aspect-ratio pillars. The material deposition was  
6 carried out in a commercial reduced-pressure chemical vapor deposition (RPCVD) reactor, thus  
7 extending the “vertical-heteroepitaxy” technique developed by using the peculiar Low-energy  
8 plasma-enhanced chemical vapor deposition reactor (LEPECVD), to widely available epitaxial  
9 tools. The growth process was thoroughly analyzed, from the formation of small initial seeds to  
10 the final coalescence into a continuous suspended layer, by means of Scanning- and  
11 Transmission electron microscopy, x-ray diffraction, and  $\mu$ -Raman spectroscopy. The pre-  
12 oxidation of the Si pillars sidewalls and the addition of hydrochloric gas in the reactants proved  
13 to be key to achieve highly selective Ge growth on the pillars top only, which, in turn, is needed  
14 to promote the formation of a continuous Ge layer.

15 Thanks to continuum growth models we were able to single out the different roles played by  
16 thermodynamics and kinetics in the deposition dynamics.

17 We believe that our findings will open the way to the low-cost realization of tens of  $\mu\text{m}$  thick  
18 heteroepitaxial layer (e.g. Ge, SiC, GaAs) on Si having high crystal quality.

## 1 1. INTRODUCTION

2 The vertical heteroepitaxy (VHE) of Ge crystals on Si substrates patterned in  $\mu\text{m}$ -sized, high  
3 aspect ratio Si pillars, was recently demonstrated by using a Low-energy plasma-enhanced  
4 chemical vapor deposition (LEPECVD) technique<sup>1, 2</sup>. By exploiting strong out-of-equilibrium  
5 conditions, obtained through high deposition rates (4 nm/s) and relatively moderate temperatures  
6 ( $\sim 500^\circ\text{C}$ ), the VHE allows for the growth of high quality Ge crystals featuring several  $\mu\text{m}$   
7 heights. These heterostructures can be of interest in view of possible applications because of  
8 some superior properties of Ge with respect to those obtained in deposition on bare Si(001)  
9 wafers. In fact, the high aspect ratio of the VHE Ge crystal allows for the almost complete  
10 relaxation of the thermal stress<sup>3</sup>, thus avoiding wafer bending and cracking. Moreover, threading  
11 dislocations (TD) in the active (top) part of the Ge crystal can be completely eliminated either by  
12 lateral expulsion (as in aspect-ratio trapping<sup>4</sup>) or by bending produced by faceted growth<sup>5</sup>. Very  
13 recently, the possibility to eliminate dislocations by a suitable compositional grading of the VHE  
14 has also been demonstrated<sup>6, 7</sup>.

15 These features, together with the “self-pixelation” induced by the ordered array of Si pillars,  
16 open interesting technological perspectives, e.g. in the development of next-generation infrared  
17 and x-ray detectors<sup>8, 9</sup>. On the other hand, other applications (e.g. in microelectronics) require  
18 continuous two-dimensional (2D) heterolayers. In order to respond also to these needs, it was  
19 recently shown that it is possible to trigger coalescence of adjacent VHE pillars into a continuum  
20 film by post-growth annealing<sup>10</sup>, or by suitably modifying the growth conditions<sup>11</sup>. This leads to  
21  $\mu\text{m}$ -thick Ge films, suspended on the Si pillar array underneath. If the film is divided in 100-300  
22  $\mu\text{m}$ -wide patches, rather than covering the whole wafer, a significant thermal strain relaxation of  
23 the Ge layer is provided by the tilting of the Si pillars<sup>12</sup>.

1 So far, VHE of Ge on micron-sized pillars was achieved only using a LEPECVD reactor. The  
2 peculiarity of the technique has surely limited the popularity of the approach, slowing down  
3 research in this field.

4 In this work, we show that growth of isolated Ge crystals and of a suspended Ge layer on  $\mu\text{m}$ -  
5 sized Si pillars can also be achieved using a commercial reduced-pressure CVD (RPCVD)  
6 reactor, by exploiting a newly developed deposition procedure, involving pre-oxidation of the Si  
7 pillar sidewalls and the addition of HCl in the reactant mixture. These two factors promote the  
8 selective growth of Ge on the pillars top, a key feature for the subsequent development of  $\mu\text{m}$ -  
9 sized Ge faceted crystals, and, eventually, to the formation of a continuous, suspended Ge film.  
10 A close comparison between experimental results and theoretical simulations was carried out,  
11 allowing us to thoroughly describe the growth dynamics at each stage of the growth and to single  
12 out the different contributions of thermodynamics and kinetics.

13 **The successful realization of the VHE using RPCVD, the workhorse of microelectronic**  
14 **industry, opens new routes to its exploitation in the field of substrate engineering, including**  
15 **the much sought after heterointegration of III-V materials on Si, as well as Ge integration**  
16 **on the mainstreamed Si platform for various applications like e.g. high-mobility CMOS**  
17 **transistors<sup>13</sup>, memories<sup>14</sup>, thermoelectric<sup>15</sup>, solar cells<sup>16</sup>, and monolithic integration of**  
18 **photonics with CMOS technology<sup>17</sup>.**

## 19 2. EXPERIMENTAL SECTION

20 **Sample preparation.** Si(001) 200mm wafers were covered with a hardmask, consisting of 10 nm  
21 thermal silicon oxide ( $\text{SiO}_2$ ) and 150 nm silicon nitride ( $\text{Si}_3\text{N}_4$ ) deposited by a low-pressure chemical  
22 vapor deposition (LPCVD) batch reactor. Lithographical patterning by an i-liner process, reactive  
23 ion-etching (RIE) and pulsed RIE etching (Bosch process) were used to etch deep into the Si wafer.

1 We realized different “block” arrays (e.g.  $200 \times 200 \mu\text{m}^2$ ) of  $1 \times 1 \mu\text{m}^2$  (SUB1) and  $2 \times 2 \mu\text{m}^2$  (SUB2)  
2 Si pillars,  $8 \mu\text{m}$  tall, with  $1 \mu\text{m}$  wide spacing. After resist ashing and Piranha-cleaning, the sidewalls  
3 of the created Si pillars were oxidized by  $100 \text{ nm}$  thermal  $\text{SiO}_2$  using LPCVD. Finally, the  
4 hardmask on top of the Si pillars was removed by wet chemistry using hydrofluoric acid and  
5 phosphoric acid as etchants. After wet chemistry, the sidewalls of the Si pillars were still covered  
6 with  $80 \text{ nm}$ -thick  $\text{SiO}_2$ -layer while the top facet was left oxide free. Typical results are displayed  
7 in Fig. 1(a, b).

8 The selective Ge growth was carried out in an ASM Epsilon 2000 RPCVD single wafer  
9 system. Prior to the growth, the samples were cleaned in standard RCA solution combined with a  
10 HF dip last clean. Afterwards, the samples were immediately loaded into the RPCVD growth  
11 chamber and baked out at  $1000^\circ\text{C}$  for  $30 \text{ sec}$  in order to remove remaining native oxide and  
12 moisture.

13 **Experimental characterization.** For analysis of the surface topography, we used a Zeiss  
14 Merlin scanning electron microscope (SEM) operating at  $1.5 \text{ kV}$  and a Bruker InnoVa Atomic  
15 force microscope (AFM), working in tapping mode.

16 The structural quality was investigated by Transmission electron microscopy (TEM) using a  
17 FEI Tecnai Osiris operating at  $200 \text{ kV}$ . TEM lamellas were prepared by milling and undercutting  
18 processes using a Zeiss NVision 40 Focused ion beam operating at up to  $30 \text{ kV}$ .

19 X-ray diffraction (XRD) measurements were performed using a SmartLab diffractometer  
20 from Rigaku equipped with a  $9 \text{ kW}$  rotating anode Cu source ( $\text{Cu-K}_\alpha = 0.1541 \text{ nm}$ ).  $\mu$ -Raman  
21 measurements were carried out using a Renishaw inVia microscope in backscattering geometry  
22 with  $633 \text{ nm}$  Helium-Neon red laser,  $1800 \text{ lines/mm}$  grating and  $\times 50$  objective with numerical  
23 aperture of  $0.75$ , which results in a laser spot size of  $\approx 520 \text{ nm}$  in diameter and a Ge penetration

1 depth of  $\approx 32$  nm. Each scan was calibrated by the position of the Si-Si vibration of Si(001) bulk  
 2 crystal references set to  $520.7 \text{ cm}^{-1}$ .

3 **Phase-field simulations.** A phase-field approach is exploited<sup>18</sup>, allowing for a natural  
 4 description of the complex dynamics of coalescence observed between the pristine islands in the  
 5 early stages of the growth. This is possible thanks to the implicit description of the crystal  
 6 surfaces, based on the phase-field function  $\varphi$ , assuming value 1 within the solid and 0 in the  
 7 vacuum region. A smooth transition at the interfaces between these two phases, provides a  
 8 diffused description of the free surface, nominally localized at the  $\varphi=0.5$  isoline. The evolution  
 9 of the growth front is described within a simple evaporation/condensation model by solving the  
 10 Allen-Cahn equation  $\partial\varphi/\partial t = -\delta F/\delta\varphi$ . The free energy  $F$  takes the form of a Ginzburg-  
 11 Landau functional<sup>18</sup>

$$12 \quad F = \int_V \gamma(\hat{\mathbf{n}}) \left[ \frac{\epsilon}{2} |\nabla\varphi|^2 + \frac{1}{\epsilon} W(\varphi) \right] + \frac{1}{\epsilon} S(\varphi) d\mathbf{x}$$

13 with  $\epsilon$  a measure of the width of the diffused interface and  $\gamma$  the surface energy density,  
 14 eventually dependent on the local profile orientation  $\hat{\mathbf{n}}$ . A double-well potential  $W(\varphi) =$   
 15  $18\varphi^2(1 - \varphi)^2$  is present to enforce the stability of the solid and vacuum phases, i.e. the minima  
 16 of  $W$ . The difference in energy between these two bulk phases  $\Delta\mu^0 = \mu_v^0 - \mu_s^0$  is accounted by  
 17 the last term  $S(\varphi) = \Delta\mu^0 [1 - \varphi^3(6\varphi^2 - 15\varphi + 10)]$ . Here it is assumed that only surface  
 18 energy contributes to the chemical potential. Indeed, the elastic contribution due to the Ge/Si  
 19 lattice misfit is neglected by considering as initial state islands large enough to be plastically  
 20 relaxed (*see Results and Discussion part below*). As bulk diffusion is not active at the present  
 21 growth temperature<sup>19</sup>, we also neglected Si/Ge intermixing, expected only at the very early  
 22 stages of the island formation, possibly proceeding our initial state. Surface anisotropy is

1 included by considering a continuous surface energy density function  $\gamma(\hat{\mathbf{n}})$  as in Ref<sup>20</sup>, with  
2 minima along the orientations of the typical facets of Ge, i.e. {001}, {113}, {111}, {110}, and  
3 the values are taken from the literature<sup>21</sup> following the procedure reported in Ref.<sup>22</sup>. The partial  
4 differential equations of the model are numerically solved by Finite Element Method (FEM),  
5 exploiting the AMDiS toolbox<sup>23, 24</sup>. In particular, a semi-implicit integration scheme and space-  
6 adaptive meshing are considered for efficiency. To reduce the computational cost further, we  
7 simulated a single pillar only with mirror boundary conditions. The initial profile consists of a  
8 distribution of 50 half-ellipsoidal islands, with random positions and axis lengths, laying on the  
9 top surface of the Si pillar. The latter is represented by a simple parallelepiped shape, carved  
10 away from the simulation cell, with Neumann boundary conditions at its sides. The cell size is  
11 set to match the experimental pattern.

### 12 3. RESULTS AND DISCUSSION

13 Since SEM images (not shown) evidenced that the selective deposition of Ge on both SUB1  
14 and SUB2 substrates follow a very similar behaviour, we first focused here on the growth  
15 dynamics on SUB2. A detailed comparison between the two substrates will be resumed in the  
16 following of the manuscript when discussing the formation of the continuous Ge layer. In Fig.  
17 1(c-e), we display the SEM images of samples in which a 60 min deposition was performed with  
18 different recipes. **The first growth attempt was carried out using a “standard” two-**  
19 **temperature (300°C/550°C) RPCVD process using GeH<sub>4</sub> as reactant gas with H<sub>2</sub>, which**  
20 **lead to high quality Ge/Si(001) relaxed heterolayers<sup>25</sup> and was close to the process**  
21 **temperature conditions of the reported LEPECVD process (~ 500°C)<sup>1,2</sup>.** Figure 1(c) shows  
22 that, beside the formation of high quality, faceted Ge  $\mu$ -structures on top of the Si pillars, the

1 growth process resulted in the nucleation of several randomly distributed and sized Ge cluster on  
2 the SiO<sub>2</sub> pillar sidewalls (arrow). One possible explanation for this additional Ge growth on the  
3 SiO<sub>2</sub>-covered sidewalls of the pillar, which is not observed on “flat” SiO<sub>2</sub> hardmask layer<sup>21</sup>,  
4 could be the presence of local imperfections in the SiO<sub>2</sub> layer, like for instance the presence of  
5 residual Si and carbon particles after the Bosch lithographic process. **To remove potential local  
6 imperfections in the SiO<sub>2</sub> layer and to increase the selectivity of the Ge growth, we were  
7 forced to modify the process condition by eliminating the low temperature deposition and  
8 increasing the subsequent deposition temperature from 500°C, i.e. one used in LEPECVD,  
9 to 650°C, with the addition of HCl gas to the H<sub>2</sub>-GeH<sub>4</sub> gas mixture<sup>26</sup>.** The role of the HCl is  
10 to etch away low-quality material, thus favoring the selective growth of the material on the top  
11 pillar opening, as can be seen in Fig. 1(d). Here we point out that deposition carried out on pillars  
12 featuring bare Si sidewalls (i.e. not covered by SiO<sub>2</sub>), the growth resulted to be non-selective  
13 even when HCl was employed, as can be seen in Fig. 1(e). Therefore, *both* sidewall oxidation  
14 and a gas phase etchant are needed to achieve VHE in a RPCVD process.

15 *Growth is here below analyzed in detail, including intermediate stages (Fig. 2(a)) and  
16 comparisons with simulations (Fig. 2(b)), for the SUB2 case, offering the possibility to directly  
17 compare results with typical LEPECVD growth on 2×2 μm<sup>2</sup> Si pillars<sup>2</sup>.*

18 In Fig. 2(a), we display the Ge growth dynamics by showing the SEM images of samples  
19 obtained for different deposition times  $t_{dep}$ . After the first nucleation of isolated islands ( $t_{dep} \leq 1$   
20 min), a pronounced coarsening is observed, leading to a single, non-faceted μ-crystal ( $t_{dep} = 15$   
21 min). Further evolution ( $t_{dep} = 60$  min) leads to the appearance of well-defined {001}-, {113}-,  
22 {111}-, and {110}-oriented facets. For increasing deposition time (120 min) the {001} almost  
23 disappears, and the Ge μ-structure acquires a more rounded shape, hosting large {113} facets as



1 expected from Ge equilibrium crystal shape calculations<sup>27</sup>. In Fig. 3, we display a comparison of  
2 the top morphology between the two latter cases as obtained by AFM.

3 The growth process has been modelled using Phase-field simulations based on an  
4 evaporation/condensation dynamics, i.e. the motion of the growth front results from the  
5 difference between the local chemical potential  $\mu(x)$  at the surface and its reference value in the  
6 gas. Further details are given in the Experimental Section.

7 The simulation results for Ge  $\mu$ -structures, having similar volumes of the experimental ones,  
8 are reported in Fig. 2(b). The simulated growth dynamics highlights both the decrease in the total  
9 free-surface area and, with the help of a dedicated colour map, the progressive exposure of facets  
10 characterized by low surface-energy density values.

11 The comparison between experiments and simulations is particularly interesting. Up to the  
12 appearance of well-defined facets ( $t_{dep} = 60$  min) observed and predicted evolutions are very  
13 similar. **As the model directly promotes the exposure of lower-energy facets, this confirms**  
14 **that, at variance with previous LEPECVD experiments at lower temperature and higher**  
15 **deposition rates<sup>1</sup>, at least during the initial stages, the growth is mainly driven by**  
16 **thermodynamics.** The model, however, does not seem to quantitatively capture the late  
17 evolution, overestimating the size of the (001) top facet, i.e. underestimating the corresponding  
18 growth velocity with respect to other facets. It appears that the incorporation-time, orientation-  
19 independent in the model, of facets such as {113} is slower than on (001), in agreement with the  
20 conclusions drawn in Refs.<sup>1,2</sup>.

21 The ratio between facet growth velocities can be estimated from the comparison between the  
22 morphology of the  $t_{dep} = 60$  min and  $t_{dep} = 120$  min samples, as determined by SEM (Fig. 2(a)).  
23 Ideally, the resulting values should be included in our phase-field growth model. This is however

1 highly non-trivial, and it is left for future work. Nonetheless, a much simpler qualitative analysis  
2 of the effect of growth velocities can be carried out. In Fig. 4(a), a tentative prediction of later  
3 stages of growth (after  $t_{dep} = 180, 240, \text{ and } 300 \text{ min}$ ) is drawn by simply assuming self-similar  
4 growth at constant growth velocities.

5 This corresponds to assuming growth to be fully determined by facets velocities, with inter-  
6 facet diffusion being kinetically frozen, thereby mimicking typical LEPECVD conditions<sup>1</sup>.  
7 Merging of adjacent pillars is predicted, leading to the formation of a fully faceted continuous  
8 film (Fig 4(b)). This regime contrasts to some extent with the predictions of the  
9 evaporation/condensation model. Indeed, if the latter simulations are carried on for longer times  
10 (90-150 min) a continuous film is still predicted, but the resulting morphology appears much  
11 smoother, as evidenced in Fig. 4(c). Moreover, the lateral enlargement is overestimated leading  
12 to merging after only  $\sim 120 \text{ min}$ .

13 Regardless the inherent discrepancy between the two theoretical predictions, both approaches  
14 strongly suggested to perform deposition for longer time, in the hope of observing partial/full  
15 merging of the Ge crystals and to clarify both kinetic and thermodynamic contributions.  
16 Following the theoretical estimate, a new sample was therefore deposited for 300 min, leading to  
17 the continuous, suspended layer morphology displayed in Fig. 5. Even if faceted features still  
18 persist in correspondence of the  $\mu$ -crystal tops, recalling the prediction of the kinetic model (Fig  
19 4(b)), we can observe strong smoothening and accumulation of material below the film (black  
20 arrow in Fig. 5(b)), as predicted by the evaporation/condensation model. A further surface  
21 smoothening could be achieved by exploiting the enhancement of the surface diffusion<sup>10, 22</sup>  
22 through extended growth-interruption/ annealing experiment which will be the subject of a  
23 follow-up study.

1 In summary, the comparison between theory and experiments reveals the important roles  
2 played by both thermodynamics (shape determined by surface-energy minimization) and kinetics  
3 (orientation-dependent incorporation times) in determining the growth of isolated Ge crystals  
4 and their eventual merging into a continuous film by RPCVD.

5 **A more direct comparison with low-temperature/high rate LEPECVD is now possible.**

6 As we have shown above, the RPCVD-VHE of Ge on Si pillars requires oxidation of the lateral  
7 sidewalls in order to prevent Ge growth in other places except the top region. In LEPECVD such  
8 “localization” is instead ensured by the very short diffusion lengths<sup>l</sup>, so that oxidation is not  
9 required. Even in the presence of oxide on the sidewalls, the Ge crystals grown by RPCVD  
10 follow a different morphological evolution. They quickly enlarge laterally, so that merging is  
11 achieved after a few microns of vertical growth only. This is in marked contrast with low-  
12 temperature LEPECVD (~500°C), where adjacent crystals were shown to develop vertical facets  
13 and to grow parallel without ever touching each other for over 50 microns<sup>l</sup>. Longer diffusion  
14 lengths in RPCVD, allowing for material redistribution are likely to cause this difference.

15 Indeed, in the Fig. 5 of Ref.<sup>11</sup>, results similar to the present ones were obtained by forcing  
16 unusually slow deposition rates and high deposition temperatures (and, thus, longer diffusion  
17 length) in LEPECVD, leading to lateral Ge-crystal merging after 2 μm of Ge deposition only.

18 After the growth procedure was successfully tested and analyzed on SUB2, we repeated the same  
19 deposition protocol on SUB1. As shown in Fig. 6(a), beside some undulations at the top free  
20 surface, a continuum film similar to that obtained on SUB2 (b) is achieved.

21 Let us finally supply a thorough characterization of the deposited material quality using TEM,  
22 XRD, and μ-Raman measurements. Close-up TEM images of the Ge region located above the Si  
23 pillars (Fig. 6(c, d)) reveal highly defective areas limited to the Si/Ge interface regions (blue arrows).

1 Only few defects, on {111} glide planes, are located at other positions in the Ge layer or even reach  
2 the surface (white arrows). It is evident that, beside misfit dislocations, the defective areas at the  
3 Si/Ge interfaces are mainly populated by stacking faults and microtwins, nucleating mostly during  
4 the first 15 min of Ge growth by coalescence of initial 3D Ge islands (see early growth state TEM  
5 images in Fig. 7). Finally, defect etching showed a threading dislocation density of  $\sim 5 \times 10^7 \text{ cm}^{-2}$ ,  
6 which compares favorably against what obtained in Ge deposition on unpatterned Si wafers if, as in  
7 the present case, cycling annealing is not used ( $\sim 8 \times 10^8 \text{ cm}^{-2}$  from Ref.<sup>25</sup>).

8 To determine the in-plane strain and the epitaxial relationship of the continuous Ge layer, we  
9 have performed XRD reciprocal space mappings (RSM) of the asymmetric Si and Ge( $\bar{2}\bar{2}4$ )  
10 reflections for Ge layer grown for  $t_{dep} = 300$  min on both SUB1 and SUB2. In Fig. 8(a, b), we can  
11 see for both samples a sharp, high intensity Si( $\bar{2}\bar{2}4$ ) signal surrounded by a broader, low  
12 intensity corona of ellipsoidal shape spreading along the [110] direction. As evidenced by  
13 Si(004) XRD  $\omega$  scans in [110] direction (Fig. 8(c, d)), the ellipsoidal-shaped corona extends for  
14  $\Delta\omega = \pm 1.3^\circ$  in the SUB1 (Fig. 8(c)) and  $\Delta\omega = \pm 0.5^\circ$  in the SUB2 cases (Fig. 8(d)), indicating an  
15 additional lattice curvature (tilt) in the Si  $\mu\text{m}$ -sized pillars. As we have discussed recently<sup>12</sup>, the  
16 thermal mismatch strain between a grown continuous Ge layer “patch” and their underlying  
17 “block” array of Si pillars is partially relaxed by an inward bending of the pillars themselves;  
18 excepting stronger bending with thinner pillars (SUB1). In conclusion, the XRD observed Si  
19 tilting here originates also from the Si pillars bending, which is larger in SUB1, and results in the  
20 shown thermal strain relaxation.

21 The in-plane strain of the coalesced Ge layer was measured to be  $\varepsilon = +0.02 \pm 0.05\%$ , for SUB1  
22 (Fig. 8(a)) and  $\varepsilon = +0.10 \pm 0.05\%$  for SUB2 (Fig. 8(b)), to be compared with the  $\varepsilon = +0.18\%$  strain  
23 expected for a Ge film grown at  $650^\circ\text{C}$  on an unpatterned substrate<sup>28</sup>.

1 The investigation of the lateral distribution of the strain relaxation over the Ge “patches” on Si  
2 pillar “block” arrays carried out by  $\mu$ -Raman spectroscopy confirms the previous analysis and shows  
3 the rather good homogeneity of the measured strain over the entire patch (see Fig. 9), a very  
4 important feature in view of potential applications. In the Ge layer grown on SUB1, the patch  
5 boundaries are slightly more relaxed due to the higher tilt of the underlying pillars there (Fig. 9(a)),  
6 while, the lesser pillar tilt allows for a decreased strain relaxation only in the more “rigid” SUB2  
7 sample (Fig. 9(b)). The average strain measured on two independent SUB1(SUB2) samples is  $\varepsilon =$   
8 +0.05% (+0.14%), in good agreement with the XRD determination, with a full-width at half  
9 maximum of the strain distribution over the whole patch equal to FWHM= 0.09% (0.045%), as can  
10 be derived from Fig. 9 (c) and (d), respectively.

#### 11 4. CONCLUSIONS

12 Isolated Ge crystals and suspended layers on micron-sized Si pillars display superior  
13 properties with respect to standard 2D layers, as they allow for fine control on thermal stress and  
14 defect distribution . Such structures were so far achieved by LEPECVD only, a rather peculiar  
15 growth technique. In this work, we have demonstrated that under suitable conditions, similar  
16 results can be obtained by exploiting a widely commercial available epitaxial tool such as  
17 RPCVD. In particular, vertical heteroepitaxial growth by RPCVD was forced by pre-oxidizing  
18 the lateral sidewalls of the pillars, and full selectivity was achieved by exploiting chlorine as  
19 etchant.

20 It was shown that a thermodynamic growth model nicely captures the first stages of growth and  
21 some general features of the grown structures, while kinetic contributions, here described by a  
22 faceted model, become more important when considering mature isolated Ge crystals, eventually  
23 leading to merging. **Despite some differences with respect to the typical morphology of the**

1 **Ge crystals grown by LEPECVD at lower temperatures and higher deposition rates, our**  
2 **results prove that also RPCVD-VHE is effective in relaxing the thermal strain via the**  
3 **compliance of the underlying patterned Si, if sufficiently thin pillars are used and thus can**  
4 **potentially be employed to deposit arbitrarily thick, crack-free heteroepitaxial layers.**

## 5 ASSOCIATED CONTENT

### 6 **Figure captions**

7 **Figure 1:** (a) SEM image of prepared  $2 \times 2 \mu\text{m}^2$  Si pillars, 8  $\mu\text{m}$  tall, with 1  $\mu\text{m}$  wide spacing. The  
8 Si pillar in the foreground was mechanically cleaved in order to display the 80 nm thick  $\text{SiO}_2$   
9 sidewall coating. The wave-like shape of the  $\text{SiO}_2$  sidewalls is typical for the Bosch process. (b)  
10 SEM image of a typical pillar-patterned substrate. (c-e) SEM images of  $2 \times 2 \mu\text{m}^2$  Si pillars after  
11 60 min Ge deposition by RPCVD (c) using a standard two-step process at  $300^\circ\text{C}/550^\circ\text{C}$  without  
12 cyclic annealing<sup>25</sup>, (d) using a one-step process at  $650^\circ\text{C}$  with HCl gas as etchant<sup>26</sup>, and (e) using  
13 a one-step process at  $650^\circ\text{C}$  with HCl gas but without  $\text{SiO}_2$ -covered sidewalls.

14 **Figure 2:** (a) SEM images of the crystal growth on SUB2. Different durations of the deposition  
15 process are considered. (b) Selected stages of a phase-field growth simulations reproducing the  
16 trend observed in experiments. The initial profile is set by a random distribution of ellipsoids,  
17 mimicking the first islands.  $\{001\}$ ,  $\{113\}$ ,  $\{111\}$ , and  $\{110\}$  facets are considered as highlighted  
18 by the colour map, showing the variation of the surface energy density  $\gamma$  along the profile.

19 **Figure 3:** AFM analysis of the top of a typical Ge crystal grown on SUB2 for (a)  $t_{dep} = 60$  min  
20 and (b)  $t_{dep} = 120$  min. Both 3D perspective views and gradient images are shown.

1 **Figure 4:** Simulations of profile evolution toward crystal coalescence in a suspended film. (a)  
2 Prediction of the facet evolution in a fully kinetic regime for an isolated crystal with growth rates  
3 extrapolated from the experimental profiles at 60 min and 120 min long deposition, overlapped  
4 as in the figure (in red and blue respectively). In particular growth rates relative to (001) are  
5  $v_{113} \approx 76\%$ ,  $v_{111} \approx 68\%$ ,  $v_{110} \approx 48\%$ . (b) Prediction of the conditions of crystal coalescence when the  
6 crystals are 1  $\mu\text{m}$  far apart, based on the calculation in panel a. (c) Extension of the phase field  
7 simulation shown in Fig. 2(b) to longer times in order to observe crystals coalescence.

8 **Figure 5:** (a) SEM view of the suspended Ge film obtained by 300 min growth on SUB2. (b)  
9 Evolution sequence reconstructed by overlapping SEM images for the crystals grown after 60  
10 min (red coloured) and 120 min (blue) with a TEM cross-section of the suspended film obtained  
11 after 300 min deposition on SUB2 (green).

12 **Figure 6:** Cross-section TEM images of coalesced, single crystalline  $\sim 1.8 \mu\text{m}$  thick Ge layers  
13 after  $t_{dep} = 300$  min Ge growth on (a) SUB1 and (b) SUB2. Black arrows indicate material growth  
14 below the film as in Fig. 5(a). Corresponding close-up images are displayed in panels (c) and (d),  
15 respectively. All images are projected along the  $\langle 1\bar{1}0 \rangle$  azimuth.

16 **Figure 7:** (a) Cross-section TEM image of defective single crystalline Ge islands after  $t_{dep} = 1$   
17 min Ge growth on  $2 \times 2 \mu\text{m}^2$  Si pillars (SUB2) as well as (b) corresponding close-up image of one  
18 selected Ge island. Images are projected along the  $\langle 1\bar{1}0 \rangle$  azimuth.

19 **Figure 8:** RSM of asymmetric  $(\bar{2}\bar{2}4)$  reflections of Si and Ge measured on a  $t_{dep} = 300$  min Ge  
20 layer grown on (a) SUB1 and (b) SUB2.  $Q_z$ -axis is parallel to (400) net plane normal and  $Q_x$ -axis  
21 is perpendicular to  $Q_z$  in the diffraction plane. The red arrows indicate the direction of full

1 relaxation in reciprocal space. Corresponding  $\omega$  scans measurements for (c) SUB1 and (d) SUB2  
2 around the Si(004) reflection in [110] direction.

3 **Figure 9:**  $\mu$ -Raman lateral strain mappings and their corresponding lateral strain histograms  
4 (average lateral strain value fitted by Gaussian function (black)) of a  $200 \times 200 \mu\text{m}^2$  block array  
5 of Si pillars overgrown by coalesced Ge layer after 300 min growth on (a, c) SUB1 and (b, d)  
6 SUB2, respectively.

## 7 AUTHOR INFORMATION

### 8 Corresponding authors

9 \*(O.S.) - for experiments. Email: skibitzki@ihp-microelectronics.com

10 \*\*(R.B.) - for theory. Email: roberto.bergamaschini@mater.unimib.it

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## 14 REFERENCES

- 15 [1] Falub, C. V.; von Känel, H.; Isa, F.; Bergamaschini, R.; Marzegalli, A.; Chrastina, D.;  
16 Isella, G.; Müller, E.; Niedermann, P.; Miglio, L. Scaling Hetero-Epitaxy from Layers to  
17 Three-Dimensional Crystals *Science* **2012**, *335*, 1330–1334.
- 18 [2] Bergamaschini, R.; Isa, F.; Falub, C. V.; Niedermann, P.; Müller, E.; Isella, G.; von Känel,  
19 H.; Miglio, L. Self-aligned Ge and SiGe three-dimensional epitaxy on dense Si pillar  
20 arrays *Surface Science Reports* **2013**, *68*, 390–417.



- 1 [3] Falub, C. V.; Meduňa, M.; Chrastina, D.; Isa, F.; Marzegalli, A.; Kreiliger, T.; Taboada, A.  
2 G.; Isella, G.; Miglio, L.; Dommann, A.; von Känel, H. Perfect crystals grown from  
3 imperfect interfaces *Scientific Reports* **2013**, *3*:2276, 1-6.
- 4 [4] Park, J.-S.; Bai, J.; Curtin, M.; Adekore, B.; Carroll, M.; Lochtefeld, A. Defect reduction of  
5 selective Ge epitaxy in trenches on Si(001) substrates using aspect ratio trapping *Appl.*  
6 *Phys. Lett.* **2007**, *90*, 052113–052115.
- 7 [5] Marzegalli, A.; Isa, F.; Groiss, H.; Müller, E.; Falub, C. V.; Taboada, A. G.; Niedermann,  
8 P.; Isella, G.; Schäffler, F.; Montalenti, F.; von Känel, H.; Miglio, L. Unexpected  
9 Dominance of Vertical Dislocations in High-Misfit Ge/Si(001) Films and Their  
10 Elimination by Deep Substrate Patterning *Adv. Mater.* **2013**, *25*, 4408–4412.
- 11 [6] Salvalaglio, M.; Montalenti, F. Fine control of plastic and elastic relaxation in Ge/Si  
12 vertical heterostructures *J. Appl. Phys.* **2014**, *116*, 104306-1–104306-9.
- 13 [7] Isa, F.; Salvalaglio, M.; Dasilva, Y. A. R.; Meduňa, M.; Barget, M.; Jung, A.; Kreiliger, T.;  
14 Isella, G.; Erni, R.; Pezzoli, F.; Bonera, E.; Niedermann, P.; Gröning, P.; Montalenti, F.;  
15 von Känel, H. Highly Mismatched, Dislocation-Free SiGe/Si Heterostructures *Adv. Mater.*  
16 **2016**, *28*, 884–888.
- 17 [8] Michel, J.; Liu, J.; Kimerling, L.C. High-performance Ge-on-Si photodetectors *Nat.*  
18 *Photonics* **2010**, *4*, 527-534.
- 19 [9] Kreiliger, T.; Falub, C.V.; Isa, F.; Isella, G.; Chrastina, D.; Bergamaschini, R.; Marzegalli,  
20 A. Kaufmann, R.; Niedermann, P.; Neels, A.; Müller, E.; Meduňa, M.; Dommann, A.;  
21 Miglio, L.; von Känel, H. Epitaxial Ge-crystal arrays for X-ray detection *J. Instrum.* **2014**,  
22 *9*, C03019.

- 1 [10] Salvalaglio, M.; Bergamaschini, R.; Isa, F.; Scaccabarozzi, A.; Isella, G.; Backofen, R.;  
2 Voigt, A.; Montalenti, F.; Capellini, G.; Schroeder, T.; von Känel, H.; Miglio, L.  
3 Engineered Coalescence by Annealing 3D Ge Microstructures into High-Quality  
4 Suspended Layers on Si *ACS Appl. Mater. Interfaces* 2015, 7, 19219–19225.
- 5 [11] Bergamaschini, R.; Salvalaglio, M.; Scaccabarozzi, A.; Isa, F.; Falub, C. V.; Isella, G.; von  
6 Känel, H.; Montalenti, F.; Miglio, L. Temperature-controlled coalescence during the  
7 growth of Ge crystals on deeply patterned Si substrates *J. Cryst. Growth* 2016, 440, 86–95.
- 8 [12] Marzegalli, A.; Cortinovis, A.; Basset, F.B.; Bonera, E.; Pezzoli, F.; Scaccabarozzi, A.; Isa,  
9 F.; Isella, G.; Zaumseil, P.; Capellini, G.; Schroeder, T.; Miglio, L. Exceptional thermal  
10 strain reduction in Ge suspended layers on Si by a tilting pillar architecture (*submitted*).
- 11 [13] Lee, M. L.; Fitzgerald, E. A.; Bulsara, M. T.; Currie, M. T.; Lochtefeld, A. Strained Si,  
12 SiGe, and Ge Channels for High-Mobility Metal-Oxide-Semiconductor Field-Effect  
13 Transistors. *J. Appl. Phys.* 2005, 97, 011101.
- 14 [14] Chang, T.-C.; Jian, F.-Y.; Chen, S.-C.; Tsai, Y.-T. Developments in Nanocrystal Memory.  
15 *Mater. Today* 2011, 14, 608–615.
- 16 [15] Mingo, N.; Hauser, D.; Kobayashi, N. P.; Plissonnier, M.; Shakouri, A. Nanoparticle-in-  
17 Alloy” Approach to Efficient Thermoelectrics: Silicides in SiGe. *Nano Lett.* 2009, 9,  
18 711–715.
- 19 [16] Soref, R. The Past, Present, and Future of Silicon Photonics. *IEEE J. Sel. Top. Quantum*  
20 *Electron.* 2006, 12, 1678–1687.
- 21 [17] Olson, J. M.; Friedman, D. J.; Kurtz, S. High-Efficiency III–V Multijunction Solar Cells.  
22 In *Handbook of Photovoltaic Science and Engineering*, 2nd ed.; Luque, A., Hegedus, S.,  
23 Eds.; John Wiley & Sons: New York, 2010; Chapter 9, pp 360–408.

- 1 [18] Li, B.; Lowengrub, J.; Voigt, A. Geometric evolution laws for thin crystalline films:  
2 modeling and numerics *Commun. Comput. Phys.* **2009**, *6*, 433-482.
- 3 [19] Uberuaga, B. P.; Leskovar, M.; Smith, A. P.; Jonsson, H.; Olmstead, M. Diffusion of Ge  
4 below the Si(100) Surface: Theory and Experiment *Phys. Rev. Lett.* **2000**, *84*, 2441-2444.
- 5 [20] Salvalaglio, M.; Backofen, R.; Bergamaschini, R.; Montalenti, F.; Voigt, A. Faceting of  
6 Equilibrium and Metastable Nanostructures: A Phase-Field Model of Surface Diffusion  
7 Tackling Realistic Shapes *Cryst. Growth Des.* **2015**, *15*, 2787- 2794.
- 8 [21] Gai, Z.; Yang, W.S.; Zhao, R.G.; Sakurai, T. Macroscopic and nanoscale faceting of  
9 germanium surfaces *Phys. Rev. B* **1999**, *59*, 15230-15239.
- 10 [22] Salvalaglio, M.; Bergamaschini, R.; Backofen, R.; Voigt, A., Montalenti, F.; Miglio, L.  
11 Phase-field simulations of faceted Ge/Si-crystal arrays, merging into a suspended film  
12 *Applied Surface Science* **2016**, (in press) doi:10.1016/j.apsusc.2016.05.075.
- 13 [23] Vey, S.; Voigt, A. AMDiS - adaptive multidimensional simulations *Comput. Vis. Sci.*  
14 **2007**, *10*, 57-67.
- 15 [24] Witkowski, T.; Ling, S.; Praetorius, S.; Voigt, A. Software concepts and numerical  
16 algorithms for a scalable adaptive parallel finite element method *Adv. Comput. Math.*  
17 **2015**, *41*, 1145-1177.
- 18 [25] Yamamoto, Y.; Zaumseil, P.; Arguirov, T.; Kittler, M.; Tillack, B. Low threading  
19 dislocation density Ge deposited on Si (1 0 0) using RPCVD *Solid-State Electron.* **2011**,  
20 **60**, 2-6.
- 21 [26] Yamamoto, Y.; Schubert, M. A.; Reich, C.; Tillack, B. Selective Lateral Germanium  
22 Growth for Local GeOI Fabrication *ECS J. Solid State Sci. Technol.* **2014**, *3*, P353-P356.

- 1 [27] Stekolnikov, A.A.; Bechstedt, F. Shape of free and constrained group-IV crystallites:  
2 Influence of surface energies *Phys. Rev. B* **2005**, *72*, 125326-1–125326-9.
- 3 [28] Capellini, G.; De Seta, M; Zaumseil, P.; Kozlowski, G.; Schroeder T. High temperature x-  
4 ray diffraction measurements on Ge/Si(001) heterostructures: A study on the residual  
5 tensile strain *J. Appl. Phys.* **2012**, *111*, 073518-1–073518-6.