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Very low temperature growth of GeSi alloys with digermane, disilane and dichlorosilane

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Abstract: GeSn / GeSi multi quantum wells with (i) high Sn content, direct bandgap GeSn wells and (ii) GeSi barriers with Si contents in the few % - 30% range might be of use in optoelectronics. As GeSn has to be grown in the 300°C–375°C range (to avoid Sn segregation/precipitation), GeSi barriers should also be grown in that temperature range. GeSi might also be used to passivate, at low temperatures, the surface of Ge-rich imagers and photo-detectors. Thanks to X-Ray Reflectivity (thickness) and X-Ray Diffraction (Si content), I have therefore explored, in a 200mm Chemical Vapour Deposition tool, the 100 Torr growth of tens of nm thick GeSi layers on Ge(001) buffers. Precursor gases were Ge₂H₆ (Ge), SiH₂Cl₂ and/or Si₂H₆ (Si). Whatever the chemistry, a temperature increase in the 350°C–500°C range resulted in an increase, (a stabilization) then a decrease of the GeSi growth rate. Meanwhile, the Si content increased almost linearly with the temperature. For given Si and Ge flows, GeSi growth rates were higher and Si contents lower with SiH₂Cl₂ than with Si₂H₆. Adding SiH₂Cl₂ to Si₂H₆ had, quite surprisingly, almost no impact on the GeSi growth kinetics, which was mainly governed by the Si₂H₆ flow. With high precursor flows, I succeeded in having, with Ge₂H₆ and SiH₂Cl₂, GeSi growth rates increasing from 2 up to 32 nm min⁻¹ as the temperature increased from 325°C up to 375°C, with a Si content close to 7.5%. Growth rates increased from 0.6 up to 19 nm min⁻¹ and Si contents decreased from 24 down to 22% over the same temperature range with Ge₂H₆, SiH₂Cl₂ and Si₂H₆.

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1 - Introduction

We have studied a few years ago the low temperature epitaxy of pure Ge and of Ge-rich SiGe alloys in a 200 mm industrial Reduced Pressure - Chemical Vapor Deposition (RP-CVD) tool [1]. We first of all benchmarked germane (GeH_4) and digermane (Ge_2H_6) for the growth of pure Ge. Using Ge_2H_6 instead of GeH_4 enabled us to dramatically increase the Ge growth rate at temperatures 425 °C and lower. We also evaluated, at 400 °C, 100 Torr, the impact of the GeH_4 or Ge_2H_6 mass-flow on the Ge growth rate. For the same Ge flow, the higher surface reactivity of digermane yielded roughly five times higher growth rates than with germane. We then combined digermane with disilane (Si_2H_6) or dichlorosilane (SiH_2Cl_2) in order to study the GeSi growth kinetics at 475 °C, 100 Torr. While the SiH_2Cl_2 mass-flow did not have any clear influence on the GeSi growth rate (with a 14 nm min⁻¹ mean value, then, i.e. half that of pure Ge with the same digermane flow), a Si_2H_6 mass-flow increase resulted in a slight GeSi growth rate increase (from 11 nm min⁻¹ up to 14 nm min⁻¹). Using dichlorosilane instead of disilane resulted in definitely lower Si concentrations, in the 18% - 23% range compared to the 47%–61% range, respectively.

Being able to grow GeSi alloys with Si contents in the few % - 30% range at temperatures significantly lower than 475°C would be interesting for a lot of applications. Ge/GeSi Multi Quantum Wells (MQWs) grown on top of Ge-rich SiGe virtual substrates can for instance be used for the fabrication of optical modulators, photodetectors and light emitters [2]. Ge/GeSi MQWs could be the core of terahertz quantum cascade lasers [3]. GeSi layers grown at temperatures lower than or equal to 350°C could be used, instead of SiGeSn ternaries, as the confinement barriers in GeSi/GeSn MQWs and Double Hetero-Structures for Mid-Infra-Red lasers [4-5]. Provided that they could be grown selectively in cavities on each side of Ge p-type Metal Oxide Semiconductor Field Effect Transistors, GeSi alloys would inject uniaxial tensile strain in short gate length devices, resulting in higher electron mobilities [6-7].

While the interest of such alloys is obvious, there is, apart from Ref. [1], a lack of growth kinetics data for high Ge content GeSi alloys, at least in RP-CVD, the workhorse of the microelectronics industry. The main reason for that is, to my opinion, the scarcity of large diameter wafers with the right lattice parameter. The lattice parameter mismatch between Si(001) substrates and GeSi layers with Si contents in the few % - 30% range is indeed so large that only a few nm of the latter can be grown pseudomorphically, preventing their easy characterization with for instance X-Ray Diffraction or X-Ray Reflectivity. Bulk Ge wafers would be ideal for such investigations, but they are very expensive in 200mm and do not exist in 300mm. One thus has to master the growth of high crystalline quality, rather flat Ge Strain-Relaxed Buffers on Si(001) to have the right templates for such studies. Bauer et al. explored in 2013 the 20 Torr growth kinetics of GeSi alloys in the 350°C – 500°C range with a $\text{GeH}_4 + \text{SiH}_2\text{Cl}_2$ chemistry [8]. The following trends were identified: at a given temperature and for a fixed GeH_4 flow, the

GeSi growth rate decreased sub-linearly and the Si content increased sub-linearly with the SiH_2Cl_2 mass-flow. As the temperature changed, there was, besides the expected growth rate decrease, a decrease of the Si content in the film (Fig. 1.15 of Ref. [8]). Growth rates were low, however. At 450°C , the GeSi growth rate indeed decreased from 7 down to barely 0.4 nm min^{-1} and the Si content increased from 21% up to 43% as the $\text{F}(\text{SiH}_2\text{Cl}_2)/\text{F}(\text{GeH}_4)$ mass-flow ratio increased from 1 up to 25. Along the same lines, the GeSi growth rate decreased from 60 down to 0.6 nm min^{-1} and the Si content from 27% down to 19% as the temperature decreased from 550°C down to 350°C ($\text{F}(\text{SiH}_2\text{Cl}_2)/\text{F}(\text{GeH}_4) = 1$).

As the growth rate of pure Ge from Ge_2H_6 is definitely higher than that from GeH_4 , I will, in the coming sections, explore the 100 Torr growth kinetics of GeSi at temperatures less than 500°C , the aim being to quantify the impact of the addition of SiH_2Cl_2 and/or Si_2H_6 on it and obtain reasonable growth rates at temperatures 350°C and less. GeSi / GeSn hetero-epitaxial growth would be feasible, then. Sn precipitation and surface segregation indeed prevent the use of temperatures significantly higher than 350°C for the deposition of flat, high crystalline quality GeSn layers. Temperatures closer to 300°C have to be adopted when Sn contents above 10% are targeted [9].

2 - Experimental details

A 200mm Epi Centura 5200 cluster tool from Applied Materials was used for the growths of the Ge Strain Relaxed Buffers (SRBs) and the GeSi layers on top. The $2.5 \mu\text{m}$ thick Ge SRBs were grown with GeH_4 on Si(001) in the High Temperature epitaxy chamber. A Ge “seed” layer $\sim 120 \text{ nm}$ thick was first of all grown at 400°C , 100 Torr. After a temperature ramping-up under GeH_4 (another 80 nm of Ge grown), the rest of the Ge SRB was grown at 750°C , 20 Torr. Afterwards, a short duration Thermal Cycling under H_2 was used to lower the Threading Dislocations Density down to 10^7 cm^{-2} values and have flat surfaces (the surface root mean square roughness and Z range were around 0.8 nm and 6 nm, respectively) [10]. Ge SRBs were then stored in one of the N_2 -purge load locks before the re-epitaxy of tens of nm thick, nominally pseudomorphic GeSi layers in the Low Temperature epitaxy chamber, which is equipped with pyrometers having a linear response in the $200^\circ\text{C} - 500^\circ\text{C}$ range. The growth with Ge_2H_6 (diluted at 2% in H_2), pure SiH_2Cl_2 and/or pure Si_2H_6 of those GeSi layers was conducted at 100 Torr. The flow of purified H_2 , several tens of standard litres per minute, was not changed throughout the study. H_2 was injected to (i) lower the partial pressures of unwanted impurities (such as O_2 , H_2O or CH_x compounds) that might enter the chamber which is not as tight as molecular beam epitaxy chambers, (ii) ensure that a laminar flow of gases is flowing over the wafer surface and (iii) passivate dangling bonds, notably at low temperatures, inhibiting unwanted adsorption of impurities on the surface.

X-Ray Reflectivity (XRR) experiments were performed in a fully automated Jordan-Valley tool with a convergent incident X-Ray beam and a 1024 pixel Charge-

Coupled Display detector that sampled the reflected beam over an $\sim 3.5^\circ$ range. A X'Pert Panalytical tool with a copper anticathode as the X-Ray source, a 4 bounces symmetric Ge(220) Bartels' monochromator for incident beam conditioning and another 2 bounces Ge(220) analyser crystal in front of the detector was otherwise used for the high resolution X-Ray Diffraction (XRD) measurements around the (004) order.

3 – The metrology used on the GeSi/Ge samples

As stated in Section 2, I have used XRR and XRD to gain access, at the wafer center, to the thickness and Si composition of the tens of nm thick, pseudomorphic GeSi layers grown on the 2.5 μm thick Ge SRBs (grown beforehand on Si(001) substrates). XRR and XRD curves acquired on the GeSi layers grown with Ge_2H_6 and the lowest of the two SiH_2Cl_2 mass-flows probed can be found in **Figure 1**.

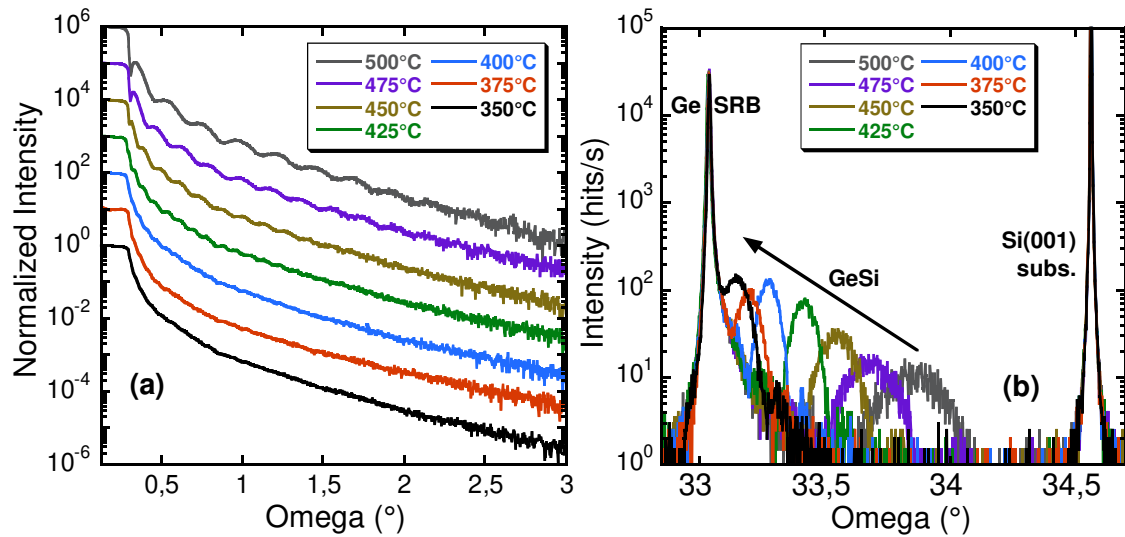


Figure 1 : (a) XRR curves and (b) Omega-2Theta scans around the (004) XRD order associated with 18 to 58 nm thick GeSi layers grown at 100 Torr with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry on Ge SRBs, themselves on Si(001). $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$, growth temperature in the 350°C – 500°C range.

As the Si content and thus the optical index difference between GeSi and Ge were high (Si has a much lower density than Ge, 2.33 g cm^{-3} compared to 5.33 g cm^{-3}), thickness fringes up to high incidence angles were present on the XRR curves of layers grown in the 425°C – 500°C range. This meant that the GeSi surfaces were flat. An AFM image typical of such surfaces can be found in Figure 10a. By contrast, such XRR thickness fringes were of low intensity or not distinguishable for some of the samples grown at 400°C and below. This was likely due to Si contents not high enough to yield meaningful density and thus optical index differences, as we will see in the following. The presence of small islands on the surface for temperatures less than 400°C might also

have reduced the amplitude of the thickness fringes (see Figures 10b-d). A Fast Fourier Transform (FFT) of the XRR curves with fringes yielded GeSi layer thicknesses. XRD, by contrast, was not hampered by small Si contents in the GeSi layers. Besides the Si(001) substrate and Ge SRB peaks located at 34.56° and 33.04° , there was always a well-defined, intense GeSi XRD peak in-between, with a thickness fringe at high incidence angles for the thickest layers, which was another sign that layers were of good crystalline quality. This peak moved towards the Ge SRB peak as the growth temperature decreased. This was due to a Si concentration decrease, as shown in Fig. 2. Fits based on the Takagi-Taupin dynamical diffraction theory of the experimental profiles yielded, with the assumption that GeSi layers were fully tensile strained on the larger lattice parameter Ge SRBs underneath, the Si content and another estimation of the thickness. Those fits took into account the fact the Ge SRBs were also slightly tensile-strained because of differences in thermal dilation coefficients between Ge and Si coming into play during the cooling-down to room temperature after growth (macroscopic degree of strain relaxation of 104%, typically [10]).

4 – Impact of SiH_2Cl_2 on the 100 Torr growth kinetics of GeSi in the 350°C – 500°C range

I have started this study by quantifying the impact of “Low” or “High” amounts of SiH_2Cl_2 (DCS) on the 100 Torr growth kinetics of GeSi in the 350°C – 500°C range. The digermene flow was half that used for GeSi growth at 475°C in Ref. [1], in order to have reasonably high Si contents at low temperatures: $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4} \Leftrightarrow 3.96 \times 10^{-4}$ in Ref. [1]. The SiH_2Cl_2 mass-flows probed, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$ or 1.125×10^{-2} , resulted in $F(\text{Si})/F(\text{Ge})$ atomic flow ratios of 6.3 or 56.7 (see **Table 1**).

The pure Ge growth rate (from Ref. [1]) and the GeSi growth rates with those mass-flows are provided as functions of the growth temperature in **Figure 2a**. The Si contents in the resulting GeSi layers are plotted in **Figure 2b**.

I will first discuss the peculiar behaviour of the pure Ge Growth Rate (GR) from Ge_2H_6 . It definitely increases with the temperature in the 325°C – 400°C range, with a $36 \text{ kcal. mol}^{-1}$ activation energy which is very close to that of the Ge-H bond strength ($37 \text{ kcal. mol}^{-1}$ [11]). Such GR, which are definitely higher than those with GeH_4 , are likely due to the ability digermene molecules have of creating their own adsorption sites on H-terminated Ge surfaces. The following mechanisms would be at play, then: the Ge–Ge bond of a digermene molecule and a surface Ge–H bond nearby break. One of the two GeH_3 fragments bonds to the surface site vacated by the H atom, which simultaneously bonds to the other GeH_3 fragment, forming gaseous GeH_4 (i.e. $\text{Ge}_2\text{H}_6(\text{g}) + \text{H}(\text{a}) \rightarrow \text{GeH}_3(\text{a}) + \text{GeH}_4(\text{g})$; (g) stands for gaseous while (a) means adsorbed) [1], [12]. At 400°C and above, the Ge growth rate reaches a plateau then decreases. Such a behaviour would be explained by a $\text{Ge}_2\text{H}_6(\text{g}) + 2\text{GeH}(\text{a}) \rightarrow 2\text{GeH}_4(\text{g}) + 2\text{Ge}(\text{s})$ alternative reaction pathway becoming predominant at the expense of the $\text{Ge}_2\text{H}_6(\text{g}) + \text{H}(\text{a}) \rightarrow \text{GeH}_3(\text{a}) + \text{GeH}_4(\text{g})$ reaction. A gradual shift to a “ GeH_4 —like” growth behavior would then occur

as the temperature increases. The same reactions, with Si instead of Ge, were used in Refs. [13-15] to explain, for Si_2H_6 , the sharp Si growth rate increase with temperature up to 575°C (with a $53 \text{ kcal. mol.}^{-1}$ activation energy close to the $47 \text{ kcal. mol.}^{-1}$ Si-H bond strength [11]), the plateau then the Si GR decrease (in the $575^\circ\text{C} - 675^\circ\text{C}$ range).

Adding SiH_2Cl_2 to Ge_2H_6 results, whatever the amount and the growth temperature, in GeSi GR which are lower than that of pure Ge, in line with Ref. [1] findings at 475°C for the same chemistry and also in line with Ref. [8] findings for $\text{GeH}_4 + \text{SiH}_2\text{Cl}_2$. This is likely due to higher Cl coverages and lower Ge coverages on GeSi surfaces with such a chlorinated chemistry. Si-Cl, Ge-Cl and Si-H bonds, which are harder to break than Ge-H bonds, would hamper growth, then (respective bond strengths: $90 \text{ kcal. mol.}^{-1}$, $51 \text{ kcal. mol.}^{-1}$ [16] and $47 \text{ kcal. mol.}^{-1}$, to be compared with $37 \text{ kcal. mol.}^{-1}$ only). HCl vapors, a by-product of DCS decomposition, might also etch Si and Ge surface atoms. Indeed, Si growth from dichlorosilane occurs as follows [17-19]:

- (i) gaseous SiH_2Cl_2 decomposes in the gaseous phase into SiCl_2 and H_2 ($\text{SiH}_2\text{Cl}_2(\text{g}) \leftrightarrow \text{SiCl}_2(\text{g}) + \text{H}_2(\text{g})$);
- (ii) gaseous SiCl_2 adsorbs on the surface ($\text{SiCl}_2(\text{g}) + _ \leftrightarrow \text{SiCl}_2(\text{a})$);
- (iii) adsorbed SiCl_2 is reduced to Si and HCl vapors by H_2 ($\text{SiCl}_2(\text{a}) + 2\text{H}_2(\text{g}) \leftrightarrow \text{Si}(\text{s}) + 2\text{HCl}(\text{g})$).

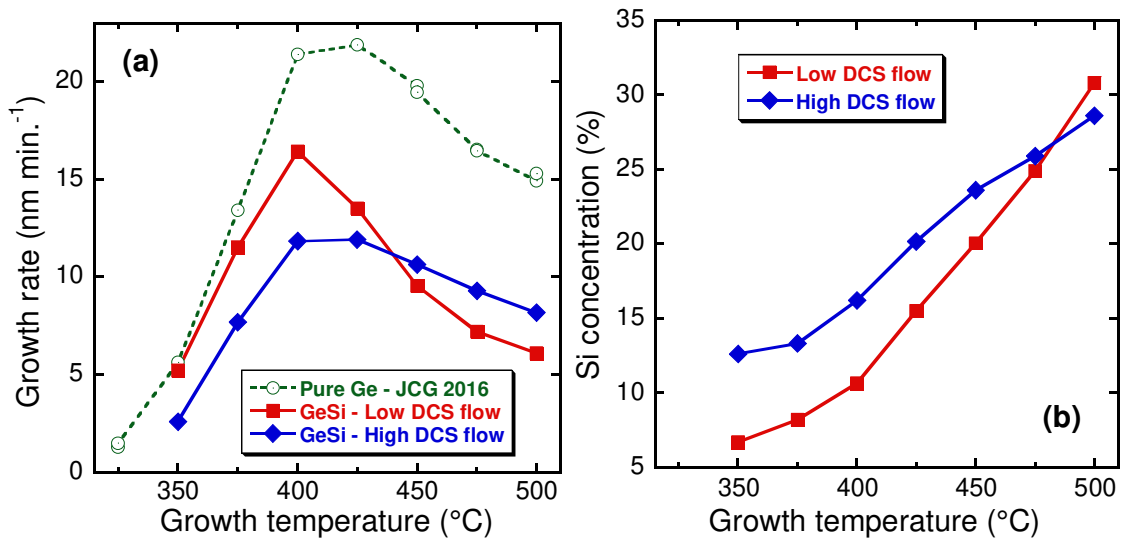


Figure 2 : (a) Growth rates and (b) Si content in GeSi layers grown at 100 Torr with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry on Ge SRBs, themselves on Si(001). $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$ or 1.125×10^{-2} (“Low” and “High” DCS flows), growth temperature in the $325^\circ\text{C} - 500^\circ\text{C}$ range.

As for pure Ge, the GeSi GR increases exponentially with the temperature in the $350^\circ\text{C} - 400^\circ\text{C}$ range, with activation energies which are lower than for pure Ge ($E_a(\text{GeSi}, \text{“Low” DCS flows}) = 26 \text{ kcal. mol.}^{-1}$ and $E_a(\text{GeSi}, \text{“High” DCS flows}) = 35 \text{ kcal. mol.}^{-1}$, to be compared with $E_a(\text{pure Ge}) = 36 \text{ kcal. mol.}^{-1}$). There is otherwise, in

that temperature range, a monotonic decrease of the growth rate as the SiH_2Cl_2 mass-flow increases, with, on average, values 85% and 53% that of pure Ge for “Low” and “High” DCS flows. The situation is more complex above 400°C, with a sharper decrease of the GeSi growth rate as the temperature increases for “Low” than for “High” DCS flows, resulting in GR which are counterintuitively higher for the later than for the former for temperatures above 425°C. The Si content in the resulting GeSi alloys increases slowly then more rapidly with the temperature, from 7% up to 31% for “Low” DCS flows and from 12% up to 29% for “High” DCS flows. The slope of that increase was faster in the former than in the latter case, which was unexpected. It resulted in Si contents which were, for “Low” DCS flows, close to or higher than for “High” DCS flows in the 475°C-500°C range. Below 475°C, Si contents were, as expected, lower for DCS flows 9 times lower.

This monotonous increase of the Si content with the temperature was not a surprise. It was indeed in line with (i) Ref. [8] findings for a $\text{GeH}_4 + \text{SiH}_2\text{Cl}_2$ chemistry and the same temperature range and (ii) Ref. [20] findings for a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ chemistry and a 450°C – 550°C range (although Si contents were much higher in the latter study).

In order to gain more insight about the growth mechanisms with such a chemistry, I have plotted in **Figure 3** the Ge and the Si growth rate components functions of temperature for pure Ge and GeSi with the two DCS flows (Si GR component = $x * \text{GeSi GR}$ and Ge GR component = $(1-x) * \text{GeSi GR}$, x being the Si content in the GeSi alloys).



Figure 3: Ge and Si growth rate components at 100 Torr functions of the growth temperature in the 325°C – 500°C range for Ge_2H_6 and $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistries. $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$ or 1.125×10^{-2} (“low” and “high” DCS flows).

Adding SiH_2Cl_2 resulted in a reduction of the Ge GR component compared to that of pure Ge whatever the temperature (same Ge_2H_6 flow). The trend is the same in all

cases: the Ge GR component increases exponentially with the temperature from 350°C up to 400°C, with activation energies very close to that of GeSi (see above). It decreases for temperatures above 400°C, at a faster pace for pure Ge and “Low” DCS flows than for “High” DCS flows. The situation is somewhat different for the Si GR components. They first of all increase exponentially with the temperature in the 350°C – 400°C range ($E_a(\text{Si GR component, “Low” DCS flows}) = 27 \text{ kcal. mol.}^{-1}$ and $E_a(\text{Si GR component, “High” DCS flows}) = 30 \text{ kcal. mol.}^{-1}$). They reach a plateau in the 425°C -500°C range, with growth rates which are barely higher for a DCS flow 9 times higher (on average, 2.4 compared to 1.9 nm min⁻¹). Such values are surprisingly high compared to the homo-epitaxial growth rate of Si from DCS, which is around 0.5 nm min⁻¹ at 650°C, 20 Torr and virtually nil below [12]. Based on that, it is surprising to reach 7-12% Si contents in GeSi alloys grown at 350°C, i.e. a temperature 300°C below that threshold.

5 – Impact of Si₂H₆ and Si₂H₆ + SiH₂Cl₂ mixtures on the 100 Torr growth kinetics of GeSi in the 350°C – 425°C range

I have continued this study by quantifying the impact of moderate amounts of SiH₂Cl₂, Si₂H₆ or mixtures of Si₂H₆ + SiH₂Cl₂ on the 100 Torr growth kinetics of GeSi in the 350°C – 425°C range. **Mixtures were evaluated in order to have an additional degree of freedom on the Si content in GeSi films. Using SiH₂Cl₂ only indeed yields low Si contents, while the use of Si₂H₆ results in high Si contents, as shown in Figures 4b and 6b. Mixing the two enables to access medium Si contents, as seen for instance in Figure 7b.** The digermane flow was the same as in Section 4, i.e. $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$. The disilane and dichlorosilane mass-flows probed, $F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 6.25 \times 10^{-4}$ and $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$, resulted in $F(\text{Si})/F(\text{Ge})$ atomic flow ratios of 6.3 (single Si precursors) or 12.6 (mixture of Si precursors): see **Table 1**. There are indeed two Si atoms in a disilane molecule, compared with one only in a dichlorosilane molecule.

The pure Ge growth rate (from Ref. [1]) and the GeSi growth rates with those chemistries and mass-flows are plotted as functions of the growth temperature in **Figure 4a**. The Si contents in the resulting GeSi layers are plotted in **Figure 4b**.

Adding Si₂H₆ or Si₂H₆ + SiH₂Cl₂ to Ge₂H₆ results, whatever the temperature, in GeSi GR which are, on average, (i) 2.3 times lower than that of pure Ge and (ii) 1.9 times lower than that of GeSi with a Ge₂H₆ + SiH₂Cl₂ chemistry. Activation energies associated with the exponential increase of the GeSi GR with the temperature in the 350°C – 400°C range were of 42 kcal. mol.⁻¹ for Ge₂H₆ + Si₂H₆ and Ge₂H₆ + Si₂H₆ + SiH₂Cl₂, to be compared with 25 kcal. mol.⁻¹ only for Ge₂H₆ + SiH₂Cl₂ and this DCS flow. A doubling of the Si flow by switching from Ge₂H₆ + Si₂H₆ to Ge₂H₆ + Si₂H₆ + SiH₂Cl₂ has almost no impact on the GeSi GR, which is barely lower with the mixture of Si precursors than with disilane only.

The Si content in the resulting GeSi alloys increases super-linearly with the temperature, from 24% up to 38% - 39.5% for Ge₂H₆ + Si₂H₆ and Ge₂H₆ + Si₂H₆ + SiH₂Cl₂. By contrast, there was an increase from 7% up to 15.5% for Ge₂H₆ + SiH₂Cl₂, a

“Low” DCS flow and that temperature range. This would be due to the relative ease Si atoms have of incorporating with Si₂H₆, which has the ability of creating its own **adsorption** site by breaking a surface Ge–H or Si–H bond (Si₂H₆(g) + H(a) → SiH₃(a) + SiH₄(g)). This results in Si contents which are, over the 350°C – 425°C range and with the same F(Si)/F(Ge) MFR of 6.3, roughly 3 times higher with Si₂H₆ than with SiH₂Cl₂. A doubling of the Si atomic flow by adding SiH₂Cl₂ to Si₂H₆ has otherwise no real impact of the Si concentration, which is almost that with Si₂H₆. The same lack of impact on GeSi GR was highlighted just above. For those GeSi layers grown at very low temperatures, the predominance Si₂H₆ has over SiH₂Cl₂ is definitely more important than for lower Ge content SiGe layers grown at 525°C, 20 Torr with a Si₂H₆ + SiH₂Cl₂ + GeH₄ chemistry [20].

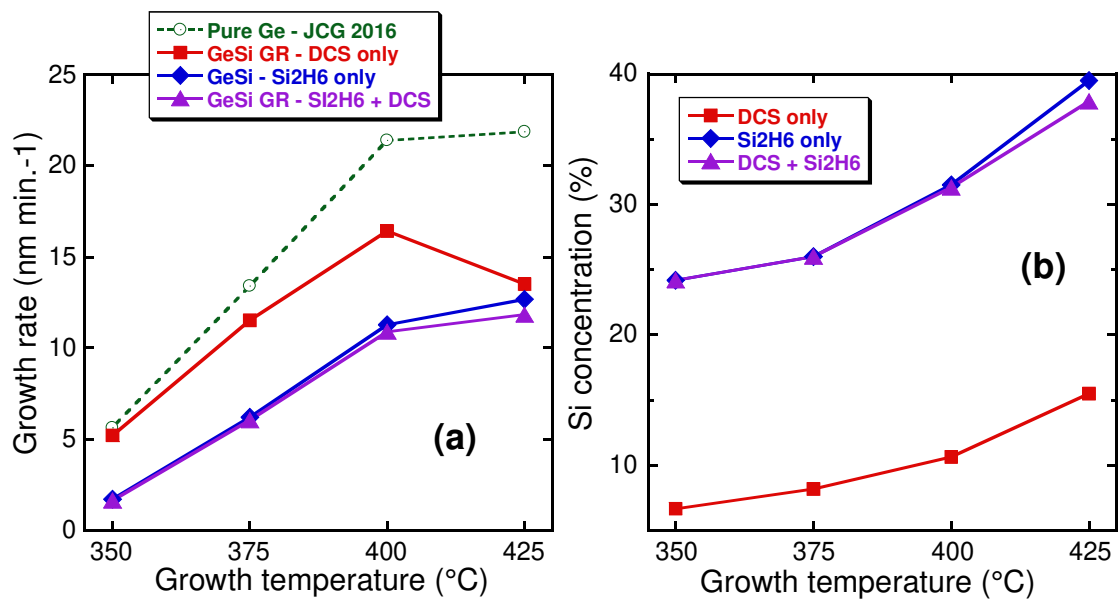


Figure 4 : (a) Growth rates and (b) Si contents in GeSi layers grown at 100 Torr with Ge₂H₆ + SiH₂Cl₂, Ge₂H₆ + Si₂H₆ or Ge₂H₆ + Si₂H₆ + SiH₂Cl₂ on Ge SRBs, themselves on Si(001). $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 1.25 \times 10^{-3}$ and/or $F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 6.25 \times 10^{-4}$, growth temperature in the 350°C – 425°C range.

The evolution with the temperature of the Si and Ge GR components can be found in **Figure 5**. It is obvious that a switch from SiH₂Cl₂ to Si₂H₆ or a mixture of Si₂H₆ + SiH₂Cl₂ results in (i) a drastic decrease of the Ge GR component and (ii) a definite increase of the Si GR component. The activation energies over the 350°C – 400°C range, 41 kcal. mol.⁻¹ for the Ge GR components and 44 kcal. mol.⁻¹ for the Si GR components, are higher for Si₂H₆ or Si₂H₆ + SiH₂Cl₂ than for SiH₂Cl₂ (26-27 kcal. mol.⁻¹). For temperatures 400°C and above, the Si GR component increases at a faster pace and the Ge GR decreases less with the formers than with the latter type of chemistry. The other interesting feature is that, maybe because of the generation of HCl during the

decomposition of SiH_2Cl_2 , Si and GR components are slightly lower with $\text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ than with Si_2H_6 .

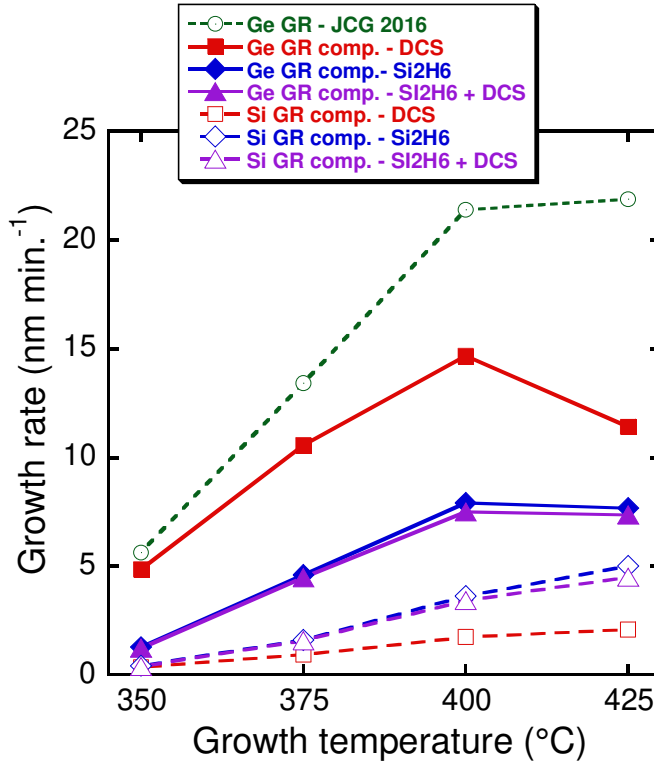


Figure 5: Ge and Si growth rate components at 100 Torr functions of the growth temperature in the 350°C – 425°C range for Ge_2H_6 , $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$, $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ and $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistries. $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 2 \times F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 1.25 \times 10^{-3}$.

6 – Impact of high flows of Si and Ge precursors on the very low temperature growth kinetics of GeSi

I have then quantified the impact of using higher Si and Ge precursor flows to boost, at temperatures less than 400°C, the GeSi growth rate, which was low indeed for the moderate flows used in Section 4. To that end, I have kept the $F(\text{Si})/F(\text{Ge})$ atomic mass-flow ratio constant at 6.3 and increased, at 350°C, 100 Torr, the Ge_2H_6 mass-flow (and thus also the Si flow) by 2, 3 and 4 (see **Table 1**). Two kinds of chemistries were investigated: $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ or $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$. In the latter case, the atomic Si flows from SiH_2Cl_2 and Si_2H_6 molecules were the same and half the overall Si flow (i.e. $F(\text{Si}_2\text{H}_6) = 0.5 \times F(\text{SiH}_2\text{Cl}_2) = 0.25 \times F(\text{Si})$), as there are two Si atoms in a disilane molecule, versus one in a dichlorosilane molecule).

GeSi growth rates and Si contents in the resulting GeSi alloys can be found in **Figure 6**. They are given as functions of the $F(\text{Si})/F(\text{H}_2)$ mass-flow ratio, $F(\text{Si})$ being equal to $F(\text{SiH}_2\text{Cl}_2) + 2 \times F(\text{Si}_2\text{H}_6)$ ($F(\text{Ge}) = 2 \times F(\text{Ge}_2\text{H}_6)$). As expected, the GeSi growth rate increases linearly with the mass-flows, from 4.6 up to 10.5 nm min^{-1} for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and from 1.6 up to 3.55 nm min^{-1} for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistry. For the same Si atomic flow, growth rates are 2.9 times higher with SiH_2Cl_2 than with $\text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ (as in Section 4). A quadrupling of the flows did not yield a

quadrupling of the GeSi growth rate, however, but a 2.2 times increase for both chemistries, instead.

Given that the $F(\text{Si})/F(\text{Ge})$ atomic mass-flow ratio was kept constant at 6.3, I would otherwise have expected the Si content in those GeSi alloys to be steady. This is to some extent the case, with a slight linear decrease of the Si content as mass-flows increase, however, from 24.2% down to 22.2% and from 8.4% down to 7.4%, respectively. Si contents from $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ are once again ~ 3 times higher than Si contents from $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$, although the Si atomic flow was the same (in line with Section 4 findings).

For $F(\text{Si})/F(\text{Ge}) = 6.3$, Si contents are, on average, equal to 0.232 and 0.079. Incoming Ge atoms are thus $6.3 / 0.232 = 27$ times more likely to incorporate in the lattice than Si atoms with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistry (13.5 times when discounting SiH_2Cl_2 molecules). Meanwhile, the Ge incorporation efficiency is $6.3 / 0.079 = 80$ times that of Si with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry.

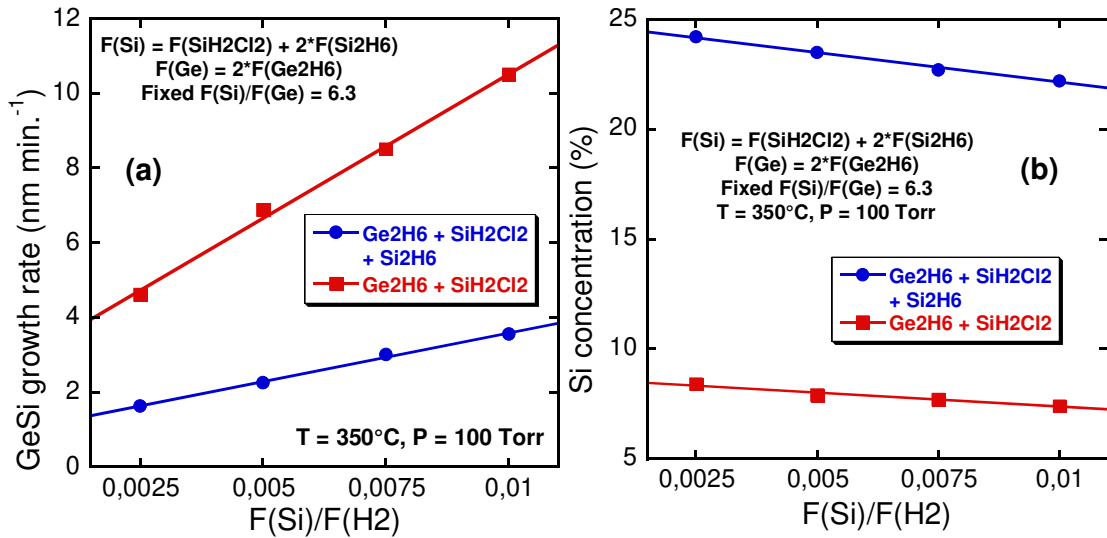


Figure 6 : (a) Growth rates and (b) Si contents in GeSi layers grown at 350°C , 100 Torr with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ or $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ on Ge SRBs, themselves on Si(001). $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 1.98 \times 10^{-4}, 3.96 \times 10^{-4}, 5.94 \times 10^{-4}$ and 7.92×10^{-4} . Pure SiH_2Cl_2 : $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 2.5 \times 10^{-3}, 5.0 \times 10^{-3}, 7.5 \times 10^{-3}$ and 10^{-2} . SiH_2Cl_2 and Si_2H_6 : $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 2 \cdot F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 1.25 \times 10^{-3}, 2.5 \times 10^{-3}, 3.75 \times 10^{-3}$ and 5.0×10^{-3} .

I have adopted the highest Ge_2H_6 mass-flow which could reproducibly be delivered in they epitaxy chamber and probed the impact of (i) varying flows of Si_2H_6 (for a fixed SiH_2Cl_2 flow) and (ii) varying flows of SiH_2Cl_2 (for a fixed Si_2H_6 flow) on the 350°C , 100 Torr growth kinetics of GeSi (see **Table 1**).

Growth rates and Si contents in the resulting GeSi alloys can be found in **Figure 7**. They are given as functions of the $F(\text{Si})/F(\text{H}_2)$ mass-flow ratio. Increasing by up to 4 the dichlorosilane flow has, for a fixed disilane flow, almost no impact on the Si content,

which stays constant at 22.3%. The GeSi growth rate decreases, however, from 4.0 down to 2.7 nm min⁻¹. By contrast, an increase by up to 4 of the disilane flow results, for a fixed dichlorosilane flow, in (i) a definite increase of the Si content, from 16.7% up to 29.7%, and (ii) a three folds decrease of the GeSi growth rate, from 5.45 down to 1.8 nm min⁻¹ only.

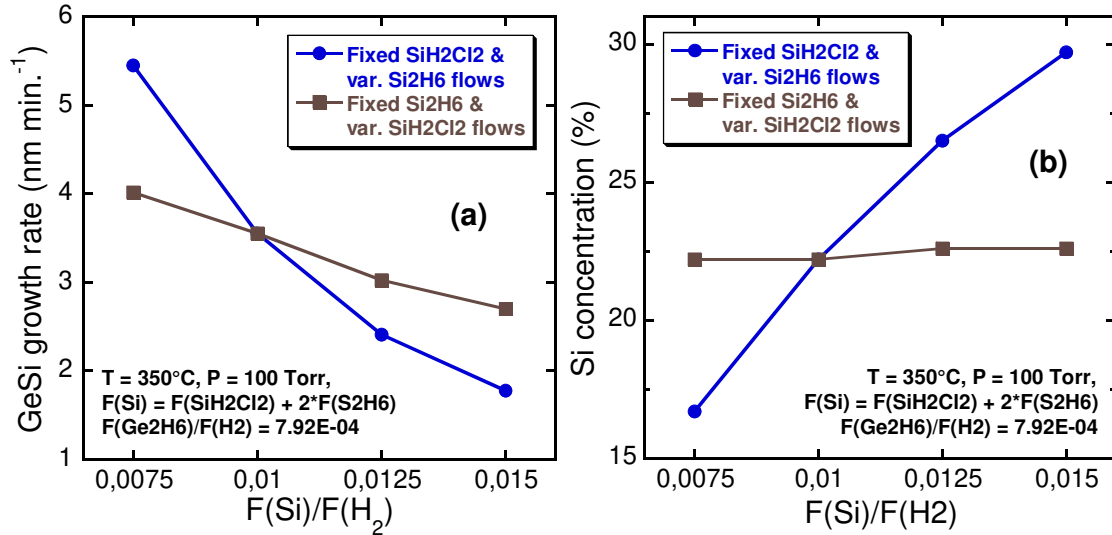


Figure 7 : (a) Growth rates and (b) Si contents in GeSi layers grown at 350°C, 100 Torr with Ge₂H₆ + Si₂H₆ + SiH₂Cl₂ on Ge SRBs, themselves on Si(001). F(Ge₂H₆)/F(H₂) = 7.92x10⁻⁴. Blue circles: fixed dichlorosilane flow (F(SiH₂Cl₂)/F(H₂) = 5.0x10⁻³), varying Si₂H₆ flows. Brown squares: fixed disilane flow (F(Si₂H₆)/F(H₂) = 2.5x10⁻³), varying SiH₂Cl₂ flows.

I thus confirm, for higher precursor flows, the trends identified in Figures 4 and 5: (i) the flow of Si₂H₆, and only that, governs Si incorporation in GeSi with such a mixture; (ii) the only impact SiH₂Cl₂ has is on growth rate, which is reduced for high flows (as if dichlorosilane was a source of gaseous HCl, an etchant, and/or if it generated, on the growing surface, a significant amount of Ge-Cl and Si-Cl bonds, which are harder to break than Ge-H bonds); (iii) the growth rate goes down as the Si content goes up, which is logical as Si-H, Ge-Cl and Si-Cl bonds are stronger than Ge-H bonds.

I have concluded this study by quantifying, for the highest digermane flow achievable in our tool, the impact of really low temperatures on GeSi growth kinetics. The F(Si)/F(Ge) atomic mass-flow ratio was, for the Ge₂H₆ + SiH₂Cl₂ and Ge₂H₆ + SiH₂Cl₂ + Si₂H₆ chemistries probed, constant and equal to 6.3 (as in Fig. 4; see **Table 1**). The atomic Si flows from SiH₂Cl₂ and Si₂H₆ molecules were, for the latter kind of chemistry, the same and half the overall Si flow (i.e. F(Si₂H₆) = 0.5xF(SiH₂Cl₂) = 0.25xF(Si)).

Growth rates and Si contents in the resulting GeSi alloys can be found in **Figure 8**. As expected, the GeSi growth rate increases exponentially with the temperature, faster

with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ than with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ ($E_a = 53 \text{ kcal. mol.}^{-1}$, to be compared with $E_a = 43 \text{ kcal. mol.}^{-1}$). Those values are higher than those in Fig. 4 for four times lower flows ($E_a = 42 \text{ kcal. mol.}^{-1}$, to be compared with $E_a = 25 \text{ kcal. mol.}^{-1}$). This might partly be due to a temperature range over which activation energies were extracted which was closer, in Fig. 4, to a high temperature regime. This likely resulted in values slightly lower than in reality, as 400°C data points started to bow downwards from pure exponentials. Fig. 8 GeSi growth rates are otherwise 2.6 times higher, on average, with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ than with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$, once again in line with Figs. 4 to 7 findings.

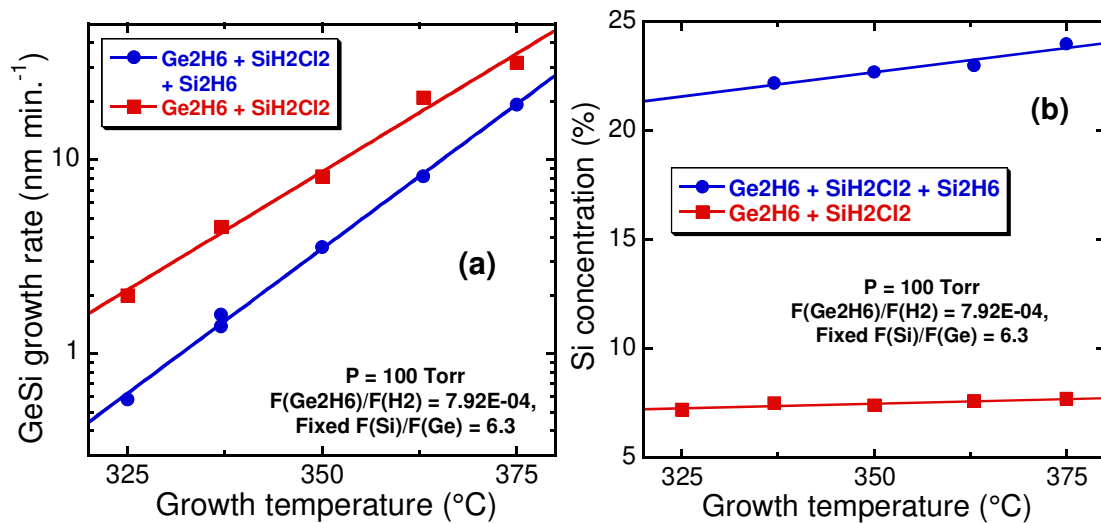


Figure 8 : (a) Growth rates and (b) Si content in GeSi layers grown at 100 Torr with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ or $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ on Ge SRBs, themselves on Si(001). $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2) = 7.92 \times 10^{-4}$. SiH_2Cl_2 only: $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 10^{-2}$. $\text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistry: $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 2 * F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 5 \times 10^{-3}$. Growth temperature in the $325^\circ\text{C} - 375^\circ\text{C}$ range.

Meanwhile, the Si contents in the resulting GeSi layers are 3 times higher, over the $325^\circ\text{C} - 375^\circ\text{C}$ range, with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ than with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ and the same $F(\text{Si})/F(\text{Ge})$ ratio of 6.3. This is fully in line with Fig. 4 findings for flows 4 times lower and higher temperatures. Those higher Si contents partly explain why activation energies associated with the exponential increase of the GeSi GR with the temperature were higher for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ than for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$: there was a higher density of more energetic Si-Cl and Si-H bonds on the surface. Si contents otherwise increase linearly with the temperature in that range, from 7.2 (325°C) up to 7.7% (375°C) for $\text{Ge}_2\text{H}_6 + \text{SiH}_2$ and from 22.2 (337°C) up to 24.0% (375°C) for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$. The increase is 5 times slower with the former than the latter type of chemistry, however ($0.09\% \Leftrightarrow 0.45\%$ gain per 10°C increase).

The Ge and Si GR components with high precursor flows are plotted in **Figure 9** as functions of the growth temperatures. They increase exponentially with the temperature, with activation energies which are similar for both components and higher for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ than for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry ($E_a = 51\text{-}53 \text{ kcal. mol.}^{-1}$, to be compared with $E_a = 43\text{-}44 \text{ kcal. mol.}^{-1}$). Using $\text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ otherwise results in Ge GR components which are, on average, 0.37 times those with SiH_2Cl_2 and Si GR components which are, on average, 1.36 times those with SiH_2Cl_2 . This reflects, once again, the relative ease Si_2H_6 molecules have of injecting Si atoms in the lattice by creating their own adsorption sites (higher Si GR components), with a Ge GR component which is then lower as, amongst other reasons, there are more Si atoms on the surface with Si-H bonds which are harder to break than Ge-H ones.

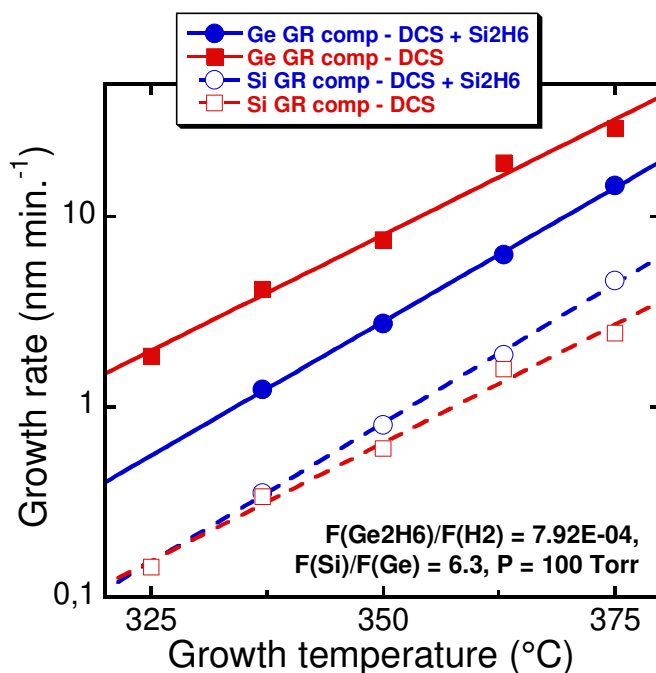


Figure 9: Ge and Si growth rate components at 100 Torr functions of the growth temperature in the 325°C – 375°C range for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ and $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistries. SiH_2Cl_2 only: $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 10^{-2}$. $\text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$: $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2) = 2 * F(\text{Si}_2\text{H}_6)/F(\text{H}_2) = 5 * 10^{-3}$.

7 – GeSi surface morphology

Before ending this paper, I will say a few words about the surface morphology of such GeSi layers. AFM images typical of the surface of GeSi layers grown with various chemistries and flows at different temperatures can be found in **Figure 10**. GeSi layers grown at temperatures 400°C and above were, irrespectively of the growth chemistry used, smooth and islands-free, with a replication of the cross-hatched morphology of the underlying Ge strain-relaxed buffers, with terraces bordered by bi-atomic steps on the slopes of small hills (**Fig. 10a**). GeSi layers grown with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry, moderate flows and temperatures below 400°C, had a few islands on the cross-hatched surface (**Fig. 10b**). Meanwhile, GeSi layers grown at temperatures below 400°C with (i) a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and high precursor flows, (ii) a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ chemistry and moderate precursor flows or (iii) a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and moderate

flows, had a larger number of islands on the surface (**Fig. 10c**). The situation was the worse on GeSi layers grown with a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and high flows, with a significant amount of islands on the surface, then (**Fig. 10d**).

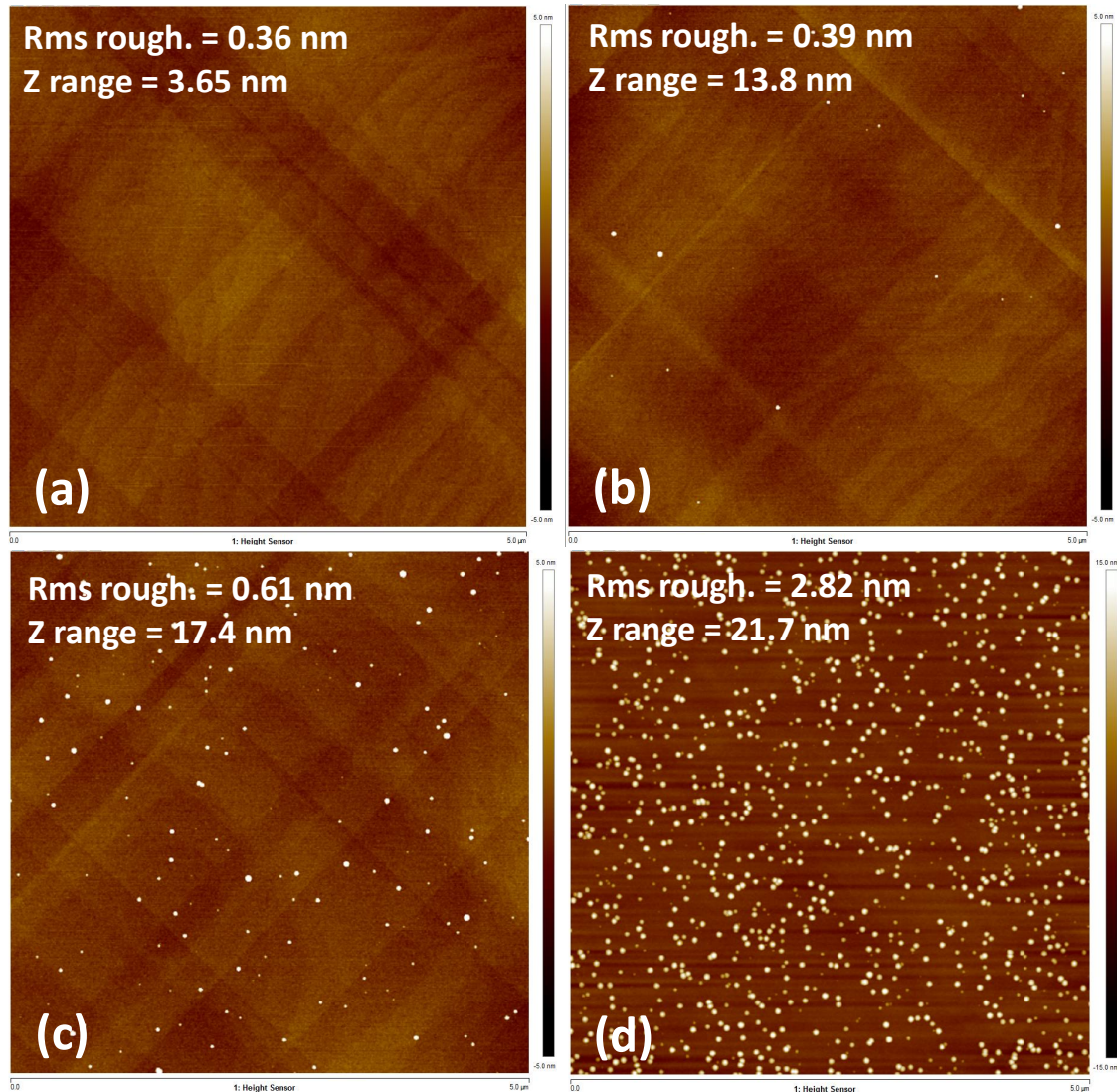


Figure 10 : $5\ \mu\text{m} * 5\ \mu\text{m}$ AFM images of the surface of (a) a 29 nm thick GeSi layer with 26% of Si grown at 475°C with moderate amounts of Ge_2H_6 and SiH_2Cl_2 , (b) a 41 nm thick GeSi layer with 7% of Si grown at 350°C with moderate amounts of Ge_2H_6 and SiH_2Cl_2 , (c) a 24 nm thick GeSi layer with 24% of Si grown at 350°C with moderate amounts of Ge_2H_6 , Si_2H_6 and SiH_2Cl_2 and, finally, (d) a 23 nm thick GeSi layer with 23% of Si grown at 350°C with high amounts of Ge_2H_6 , Si_2H_6 and SiH_2Cl_2 . Image sides along the $\langle 100 \rangle$ directions.

Those islands are probably due to growth temperatures which are too low and precursor flows (and therefore growth rates) which are too high for have perfectly monocrystalline GeSi films all over their surface. They might also be due to amorphous

inclusions in the films because of gas phase reactions during growth (for high precursor flows). Having HCl, an etchant generated during the decomposition of SiH_2Cl_2 , present in the gaseous mixture most likely helped in having smooth surfaces over the vast majority of the layers (preferential etching of growth defects after their formation). Meanwhile, the presence of vast amounts of Si_2H_6 molecules, which are more reactive on the surface and prone to gas phase reactions than SiH_2Cl_2 molecules, resulted in the formation of a larger amount of islands at temperatures less than 400°C .

A bearing analysis of Fig. 10 pictures showed that the fraction of the surface covered by islands was small, however: 0.1% only for Fig. 10(b), 0.8% for Fig. 10(c) and 7.8% for Fig. 10(d) image, one of the worse in terms of roughness. Those values are actually higher than reality, as islands are smaller than “seen” in AFM (convolution with the AFM tip, which has a 10 nm radius, typically). Those small surface coverages explain why XRR and XRD profiles were typical of smooth, pseudomorphic films: the flat portions of the films diffracted coherently (XRD) and yielded well-defined thickness fringes in XRR (monitoring of the specular signal only). Trends in Figs. 2 to 9 are logical and thus meaningful even for the highest amounts of islands (exponential growth rate increases, steady or linear fluctuations of the Si content as the temperature and/or the flows were changed and so on).

Similar islands were seen on the surface of Si (and SiGe) layers grown at low temperatures with Si_2H_6 [21], Si_3H_8 [22] and other high order Si precursors [23]. Reducing the Si precursor flow (and thus the growth rate) and switching to higher growth temperatures then helped in minimizing the island density or suppressing them, in line with Fig. 10 findings. Using Cyclic Deposition / Etch schemes enabled, thanks to the deposition of a reduced thickness and the selective etch of defects at the end of each cycle, to recover flat Si surfaces even at low temperatures [23-24]. The same strategy, with HCl (+ H_2) [16] or Cl_2 (+ N_2 or He) [25-26] as etchant gases, could be used here to have flat GeSi films at temperatures less than 400°C with the current growth data points. Adding HCl to Ge_2H_6 , SiH_2Cl_2 and/or Si_2H_6 might also help in recovering flat surfaces. It would however have an impact on growth kinetics, which would have to be quantified, then (growth rate and Si content reductions expected; adding HCl to Si_2H_6 + Ge_2H_6 indeed resulted, at 500°C , 20 Torr in lower growth rates and higher Ge contents SiGe layers [20]). **Another path might be to reduce the precursor partial pressures by lowering the chamber pressure (20 Torr only in Ref. [8]). This would potentially result in a lesser number of harmful gas phase reactions, a lower density of limited mobility adatoms on the surface and higher crystalline quality layers. GeSi growth rates would be lower, however, hindering epitaxy at temperatures 350°C and less.**

8 - Conclusions

The aim being to grow GeSi layers (with Si contents in the few % - 30% range) at temperatures significantly less than 500°C for use in various types of devices (passivation of IR imagers, GeSi/GeSn multi-quantum wells, embedded stressors in Ge pMOS devices

and so on), I have investigated the epitaxy of tens of nm thick, pseudomorphic layers on top of Ge Strain Relaxed Buffers, themselves grown on top of Si(001) substrates. The growth temperature T was in the 325°C – 500°C range and the pressure was always 100 Torr. $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$, $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ and $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistries with moderate to high flows were used for the deposition of those layers.

Adding “Low” or “High” amounts of SiH_2Cl_2 (DCS) to Ge_2H_6 resulted in GeSi growth rates, in the 350°C to 500°C range, which were lower than the growth of pure Ge with the same Ge_2H_6 flow. A switch from an exponential increase of the growth rate with the temperature (for $T \leq 400^\circ\text{C}$) to a growth rate which decreased at T increased above 400°C was evidenced. The Si content in the resulting GeSi alloys increases slowly then more rapidly with the temperature, from 7% up to 31% for “Low” DCS flows and from 12% up to 29% for “High” DCS flows.

Switching over to a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ chemistry resulted, in the 350°C - 425°C range, in GeSi growth rates which were 2 times lower and Si contents which were 3 times higher. The Si content increased monotonously with the temperature, from 24% up to 39%. Doubling the Si atomic flow by adding SiH_2Cl_2 to Si_2H_6 and Ge_2H_6 had, quite surprisingly, almost no impact on the GeSi growth kinetics, with almost the same Si contents and GeSi growth rates barely lower than those with Si_2H_6 only.

I have then quantified, for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ and $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistries, the impact of higher precursor flows on the 100 Torr GeSi growth kinetics at 350°C. The GeSi growth rate increased linearly with the mass-flows, from 4.6 up to 10.5 nm min^{-1} for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and from 1.6 up to 3.55 nm min^{-1} for a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ chemistry. Although the $F(\text{Si})/F(\text{Ge})$ atomic flow ratio was constant at 6.3, slight Si content decreases, from 24.2% down to 22.2% ($\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$) and from 8.4% down to 7.4% ($\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$), were evidenced as the individual mass-flows were quadrupled. The GeSi growth rate increased exponentially with the temperature and those high flows, faster with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$ than with $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ ($E_a = 53 \text{ kcal. mol.}^{-1}$, to be compared with $E_a = 43 \text{ kcal. mol.}^{-1}$ over the 325°C – 375°C range). Meanwhile, Si contents increased linearly, from 7.2 (325°C) up to 7.7% (375°C) for $\text{Ge}_2\text{H}_6 + \text{SiH}_2$ and from 22.2 (337°C) up to 24.0% (375°C) for $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$.

Finally, GeSi layers grown at temperatures 400°C and above were, irrespectively of the growth chemistry used, smooth, with a replication of the cross-hatched morphology of the underlying Ge strain-relaxed buffers. GeSi layers grown with a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry, moderate flows and temperatures below 400°C, had a few islands on the cross-hatched surface. Meanwhile, GeSi layers grown at temperatures below 400°C with (i) a $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and higher precursor flows, (ii) a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6$ chemistry and moderate precursor flows or (iii) a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and moderate flows, had a larger number of islands on the surface. The situation was the worse on GeSi layers grown with a $\text{Ge}_2\text{H}_6 + \text{Si}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ chemistry and high flows, with a significant amount of islands on the surface, then. Cyclic Deposition / Etch schemes, with HCl or Cl_2 periodically injected to selectively remove

islands, which are most likely the surface signature of crystalline defects or amorphous inclusions in the bulk of the layers, will likely have to be called upon to make full use of data points below 400°C. Adding HCl to the gaseous mixture might also solve this problem. Its impact on growth kinetics would have to be quantified, however.

Acknowledgements: L. Saidi, S. Rousseau, P. Roche, B. Assie and P. Nal are gratefully acknowledged for their help in operating and maintaining the Epi Centura 5200 tool.

Growth conditions (Figures)	$F(\text{Ge}_2\text{H}_6)/F(\text{H}_2)$	$F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2)$	$F(\text{Si}_2\text{H}_6)/F(\text{H}_2)$	$F(\text{Si})/F(\text{Ge})$	Growth temperature (°C)
$\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$, moderate Ge_2H_6 flow (Figs. 2 and 3)	1.98×10^{-4}	1.25×10^{-3} or 1.125×10^{-2}	0	6.3 or 56.7	350°C to 500°C
$\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$, moderate Ge_2H_6 flow (Figs. 4 and 5)	1.98×10^{-4}	1.25×10^{-3}	6.25×10^{-4}	6.3 (single Si precursors) or 12.6 (mixture of precursors)	350°C to 425°C
$\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ or $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$, increasing Ge_2H_6 flow (Fig. 6)	1.98×10^{-4} up to 7.92×10^{-4}	2.5×10^{-3} up to 10^{-2} or 1.25×10^{-3} up to 5×10^{-3}	0 or 6.25×10^{-4} up to 2.5×10^{-3}	6.3	350°C
$\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$, high Ge_2H_6 flow, varying Si flows (Fig. 7)	7.92×10^{-4}	5×10^{-3} or 2.5×10^{-3} to 10^{-2}	1.25×10^{-3} to 5×10^{-3} or 2.5×10^{-3}	9.5 up to 19	350°C
$\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2$ or $\text{Ge}_2\text{H}_6 + \text{SiH}_2\text{Cl}_2 + \text{Si}_2\text{H}_6$, high Ge_2H_6 flow (Figs. 8 and 9)	7.92×10^{-4}	10^{-2} or 5×10^{-3}	0 or 2.5×10^{-3}	6.3	325°C to 375°C

Table 1: $F(\text{Ge}_2\text{H}_6)/F(\text{H}_2)$, $F(\text{SiH}_2\text{Cl}_2)/F(\text{H}_2)$ and $F(\text{Si}_2\text{H}_6)/F(\text{H}_2)$ mass-flow ratios, $F(\text{Si})/F(\text{Ge})$ atomic mass-flow ratios and temperatures probed during this study (100 Torr epitaxial growth of GeSi alloys on Ge SRBs, themselves on Si(001)).

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