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# Assessment of the growth/etch back technique for the production of Ge strain-relaxed buffers on Si

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Thick Ge layers grown on Si(0 0 1) are handy for the production of GeOI wafers, as templates for the epitaxy of III-V and GeSn-based heterostructures and so on. Perfecting their crystalline quality would enable to fabricate suspended Ge micro-bridges with extremely high levels of tensile strain (for mid IR lasers). In this study, we have used a low temperature (400 °C)/high temperature (750 °C) approach to deposit with $GeH_4$ various thickness Ge layers in the 0.5 μm – 5 μm range. They were submitted afterwards to short duration thermal cycling under $H_2$ (in between 750 °C and 875–890 °C) to lower the Threading Dislocation Density (TDD). Some of the thickest layers were partly etched at 750 °C with gaseous HCl to recover wafer bows compatible with device processing later on. X-ray Diffraction (XRD) showed that the layers were slightly tensile-strained, with a 104.5–105.5% degree of strain relaxation irrespective of the thickness. The surface was cross-hatched, with a roughness slightly decreasing with the thickness, from 2.0 down to 0.8 nm. The TDD (from Omega scans in XRD) decreased from $8 \times 10^7\ cm^{-2}$ down to $10^7\ cm^{-2}$ as the Ge layer thickness increased from 0.5 up to 5 μm. The lack of improvement when growing 5 μm thick layers then etching a fraction of them with HCl over same thickness layers grown in a single run was at variance with Thin Solid Films 520, 3216 (2012). Low temperature HCl defect decoration confirmed those findings, with (i) a TDD decreasing from slightly more $10^7\ cm^{-2}$ down to $5 \times 10^6\ cm^{-2}$ as the Ge layer thickness increased from 1.3 up to 5 μm and (ii) no TDD hysteresis between growth and growth then HCl etch-back.

## 1. Introduction

Thick Ge Strain-Relaxed Buffers (SRBs) on Si(0 0 1) can be used for a large variety of purposes in microelectronics and optoelectronics. The top part of microns-thick Ge layers can be peeled-off from the Ge/Si stack underneath and bonded on oxidized Si using the SmartCut$^{TM}$ approach [1], resulting in Germanium-On-Insulator substrates. The latter can be used as templates for the fabrication of high mobility p-type Metal Oxide Semiconductor Field Effect Transistors [2]. The slight tensile strain present in thick Ge films on top of buried oxides can be used to fabricate highly strained suspended micro-bridges and micro-crosses [3–5]. Because of their lattice parameter, which is 4.2% higher than that of Si (5.65785 Å $\Longleftrightarrow$ 5.43105 Å) and close to that of GaAs (5.653 Å), Ge SRBs can be used as templates for the epitaxy of anti-phase boundaries-free, superior quality GaAs and InAlAs-based buffers [6–7]. The later can be used for the fabrication of high electron mobility n-type MOSFETs on III-V-On-Insulator substrates [8]. Thick Ge layers grown selectively at the end of Silicon-On-Insulator (SOI) waveguides act of the active cores of superior performance near Infra-Red photo-detectors [5,9,10]. Large area, high quality graphene 2D layers were recently deposited on Ge SRBs [11,12]. Finally, Ge SRBs are handy for the deposition of high Sn content GeSn layers which are used for the fabrication of mid-IR optically pumped lasers [13,14].

Such SRBs are typically grown on Si(0 0 1) using a Low Temperature/High Temperature approach [15], with a short duration Thermal Cycling or anneal afterwards [16] to minimize the Threading Dislocations Density (TDD). This TDD is typically around $10^7\ cm^{-2}$ for 2.5 μm thick Ge layers which are really smooth given the large lattice parameter mismatch between Si and Ge (surface root mean square roughness typically around 0.8 nm for 20 μm × 20 μm Atomic Force Microscopy images). We have shown in 2005 that the TDD exponentially decreased with the Ge thickness, which was at most 2.5 μm in Ref. [17]. The universality of such a behavior was conclusively demonstrated in the Ge/Si system and the GaAs/Si system in Ref. [18]. Yamamoto et al. extended our

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Ge/Si findings to larger thicknesses (up to 4.7 µm) in Ref. [19]. The same group published later on a very intriguing paper where they showed that initially 4.5 µm thick Ge layers thinned-down to more manageable values thanks to in-situ HCl etching were less defective than same thickness Ge layers grown in a single run [20].

Defect density minimization is a must when focusing the built-in tensile strain in suspended GeOI micro-bridges and micro-crosses (to avoid breaking when strain reaches really high values). We have thus benchmarked (i) growth and (ii) growth then etch back approaches to see if the later indeed yielded superior quality Ge buffers (and thus GeOI substrates, in the end), in line with Ref. [20] findings.

## 2. Experimental details

The Ge layers were grown in a Epi Centura Reduced Pressure-Chemical Vapor Deposition (RP-CVD) industrial cluster tool. The flow of $H_2$ carrier gas was set at a fixed value of a few tens of standard liters per minute. Germane ($GeH_4$) diluted at 2% in $H_2$ was used as the source of Ge. The $F(GeH_4)/F(H_2)$ mass-flow ratio was always equal to $7.917 \times 10^{-4}$. The Ge etch-back was conducted with pure HCl, with a $F(HCl)/F(H_2)$ mass-flow ratio of $1.875 \times 10^{-2}$. The slightly p-type doped 200 mm Si(0 0 1) substrates used were nominal (±0.25°). During growth, the wafer laid horizontally on top of a circular SiC – coated susceptor plate that rotated to improve the spatial thickness uniformity of the films. It was heated by two banks of 20 tungsten – halogen lamps (maximum power: 2 kW each) located above and below the susceptor assembly. Temperature monitoring and control was ensured through the lower pyrometer, i.e. the one which is looking at the backside of the susceptor plate on which the wafer laid.

The Ge layer thickness was determined through differential weighting using a micro-balance. Omega scans and Omega-2Theta scans around the (0 0 4) diffraction order were performed on a Panalytical X'Pert X-ray diffractometer in the so-called "triple-axis mode" (i.e. with (i) a Bartels Ge(2 2 0) 4-crystal monochromator in-between the X-ray source and the sample and (ii) a 3 bounces Ge(2 2 0) 2-crystal analyser in front of the detector). This way, (i) a monochromatic, non-divergent X-ray beam impacted the sample and (ii) the fraction of the reciprocal space probed by the detector was very small, avoiding any artificial peak enlargement due to the mosaïcity of the thick, nearly fully relaxed Ge layers. Finally, tapping-mode Atomic Force Microscopy (AFM) measurements were carried out on a Bruckers FastScan™ platform.

## 3. Experimental results

### 3.1. Growth and HCl etch-back protocol

The 0.5 µm – 2.5 µm thick Ge layers were grown on the Si(0 0 1) substrates in three steps. After a 1100 °C, 2 min $H_2$ bake (to get rid of chemical oxide through the following reaction: $SiO_2(s) + 2H_2(g) \rightarrow Si(s) + 2H_2O(g)$), a ~80 nm thick Ge layer was grown in 460 s at 400 °C, 100 Torr, in order to start from a rather flat, nearly fully relaxed Ge "seed" layer. In the second step, the temperature was ramped from 400 °C up to 750 °C (2.5 °C/s) and the growth pressure from 100 Torr down to 20 Torr while still having germane flowing into the growth chamber. Around 80 nm of Ge were deposited during the 2nd step. In the third step, a Ge layer was grown at 750 °C, 20 Torr in order to obtain the desired thickness. A 3 × (890 °C, 10 s/750 °C,10 s) Thermal Cycling was used afterwards to minimize the Threading Dislocations Density.

In order to probe thicknesses in the 3–5 µm range while avoiding quartz wall clogging (and thus flaking), we proceeded as follows: we first of all grew 2.5 µm thick cyclically annealed Ge layers thanks to the protocol described above. Those Ge SRBs were then taken out of the epitaxy chamber and stored under ultra-pure $N_2$ in the load-locks of the cluster tool. Chamber walls were thoroughly cleaned thanks to high pressure, high temperature HCl etching and the Ge layers completed after a 850 °C, 2 min $H_2$ bake using $GeH_4$ at 750 °C, 20 Torr (as before). A second 3 × (875 °C, 10 s/750 °C,10 s) Thermal Cycling was used on those really thick layers in order to lower even more the TDD [21].

To assess the interest of the HCl etch-back technique, we started from 5 µm thick Ge layers grown in two stages (see above) and etched fractions of them with a mixture of $HCl + H_2$ (also at 750 °C, 20 Torr). Germanium atoms were removed from the films through the following reaction: $Ge(s) + 2HCl(g) \rightarrow GeCl_2(g) + H_2(g)$ [22]. This etch-back was conducted in the same RP-CVD chamber used for growth [22], this just after the 2nd cyclic anneal under $H_2$ of the originally 5 µm thick Ge layers.

We have plotted in Fig. 1 the Ge thickness (in nm) as a function of the deposition or the deposition + etch-back duration (in min.). The slopes of the lines linking the experimental data points are the Ge growth rate at 750 °C, 20 Torr, i.e. 59.5 nm $min^{-1}$, or the HCl etch rate (also at 750 °C, 20 Torr), i.e. 78.7 nm $min^{-1}$. The really linear increase (or decrease) of the Ge thickness with the 750 °C process time should be highlighted. The linear extrapolation at 0 min (158 nm) corresponds to the Ge layer thickness after the 400 °C step then the temperature ramping-up (under $GeH_4$). The right-most data points are associated with etched layers which were not uniform anymore on the wafer, i.e. with a central part with some Ge on it and nothing at the edges. They were thus not taken into account when extracting the HCl etch rate, as thickness values are approximations.

### 3.2. Wafer bowing

We have quantified the wafer bow of all our samples. It is plotted as a function of Ge thickness in Fig. 2. The bow decreases linearly with the thickness, from slightly positive values (i.e. a convex shape) for bulk Si(0 0 1) wafers down to – 170 µm (i.e. a really concave shape) for 5 µm thick Ge layers. The lack of any hysteresis between growth and growth then etch-back data points should also be highlighted. Values lower than - 50 µm will be

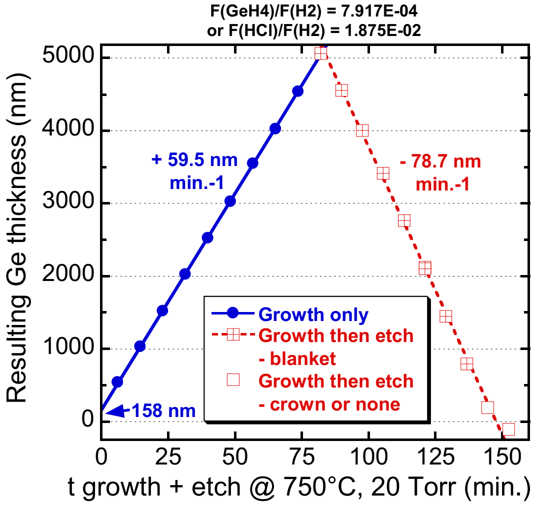

**Fig. 1.** Evolution of the mean Ge thickness on Si(0 0 1) wafers as a function of the deposition or the deposition and HCl etch duration. The slopes of the two lines are the Ge growth rate or the HCl etch rates at 750 °C, 20 Torr (59.5 and 78.7 nm $min^{-1}$, respectively).