I. INTRODUCTION

$\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ is considered a potential alternative to improve the performance of microelectronics silicon technology. $\text{Si}_{1-x}\text{Ge}_x$-based commercial heterojunction bipolar transistors (HBT) can effectively improve some figures of merit over those of standard silicon devices. Nevertheless, $\text{Si}_{1-x}\text{Ge}_x$ has some inherent inconveniences like critical thickness limitations and boron outdiffusion, and it is also rather unsuitable for process integration. To achieve further improvements in the field of group IV epilayers, it has been proposed to introduce carbon in $\text{Si}_{1-x}\text{Ge}_x$. $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ minimizes the strain in the epilayer, resulting in increased critical thickness \(^1\) and also show reduced boron outdiffusion.\(^{2,3}\) The theoretical study of HBTs based on $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ also demonstrates further improvements over the figures of merit achieved for $\text{Si}_{1-x}\text{Ge}_x$.\(^4\) This has already been demonstrated experimentally by Meyerson.\(^5\)

The complete integration of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ in CMOS (complementary metal-oxide-semiconductor) technologies has not been possible yet. The main hindrance is the metastability of the epitaxial layers when subjected to the standard high-temperature processing sequence of CMOS. On the one hand, the low solubility of carbon in silicon makes epitaxial growth difficult, as carbon tends to occupy both substitutional and interstitial positions. On the other hand, the CMOS processes involve high temperature processing so that epilayer stability is also compromised. Furthermore, studies of thermal oxidation of $\text{Si}_{1-x}\text{Ge}_x$ indicate a segregation of Ge from the oxidation front\(^6-8\) a large density of interface states.\(^9,10\) In this work, we study the benefits of including carbon in $\text{Si}_{1-x}\text{Ge}_x$ epilayers on thermal oxidation at temperatures above 900 °C. It is expected that the tensile strain induced by substitutional carbon (interstitial carbon does not contribute to strain) compensates the compressive strain induced by Ge so that the effects of thermal processing can be minimised.

Raman spectroscopy has proven useful in measuring mechanical strain in silicon-based devices and has also been used in the characterization of as-grown $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ epilayers. There is fairly good correlation between the Raman and the measured strain in $\text{Si}_{1-x}\text{Ge}_x$. They are empirically described\(^11,12\)

\[ \kappa_{\text{Si-Si}}(x) = 520 \text{ cm}^{-1} - 68x - 830\epsilon_p(x), \]  

\[ \kappa_{\text{Si-Ge}}(x) = 400.5 \text{ cm}^{-1} - 14.2x - 575\epsilon_p(x), \]  

\[ \kappa_{\text{Ge-Ge}}(x) = 282.5 \text{ cm}^{-1} - 16x - 384\epsilon_p(x), \]  

where $\kappa$ is the Raman shift in cm\(^{-1}\), $x$ is the Ge fraction of $\text{Si}_{1-x}\text{Ge}_x$, and

\[ \epsilon_p(x) = \frac{a_{||} - a_{\text{SiGe}}}{a_{\text{SiGe}}} \]  

is the mismatch between the epilayer and the substrate ($a_{||}$ and $a_{\text{SiGe}}$ are the parallel lattice and the unstrained $\text{Si}_{1-x}\text{Ge}_x$ lattice parameters). The first terms in Eqs. (1)-(3)
are the vibrational frequencies of the different modes. The second terms show the linear dependence of the lattice strain with Ge concentration and were found using data fitting. The third terms in Eqs. (1)-(3) are the result of the strain between the epitaxial layer and the substrate. The effects of strain in Si$_{1-x-y}$Ge$_x$C$_y$ due to carbon concentration have also been studied and are found to vary linearly with substitutional carbon content. Rücker and Methfensel propose an additional term for the Si-Si band: $\nu = 210$ cm$^{-1}$.13

Expressions (1)-(3) confirm a linear relationship between composition and epitaxial strain for both germanium and carbon, because of Vegard’s law. The presence of Ge in unstrained epilayers shifts Si–Si bonds toward lower frequencies, while carbon has the opposite effect. The shift toward higher frequencies indicates increasing compressive strain in the layer whereas decreasing frequency correlates to decreasing compressive strain, or the onset of tensile strain. Using Raman spectroscopy we can measure the evolution of strain during the oxidation process as a function of the initial epilayer composition.

To separate the effects of thermal processing on the layer considered up to now from the effects on the oxide, we use Fourier transform infrared (FTIR) spectroscopy to evaluate the oxide, as Raman cannot measure these amorphous layers well enough. The FTIR vibrational modes of the oxide bonds are well defined and characterized.14 The shifts may depend on different parameters, as oxide thickness, image charge effects, film inhomogeneity, and oxide stress.15 We focus here on the dependence of the asymmetric stretching (mode TO$_3$) as a function of oxide stress.

II. EXPERIMENT

Samples with compositions from $x=0.1-0.6$ of Ge and $y=6\times10^{-4}-0.05$ of C were studied. The compositions and thicknesses of the as-grown epilayers were measured by Rutherford backscattering spectroscopy (RBS) and x-ray diffraction (XRD). Results are described in Table I. Epitaxy was accomplished by atmospheric pressure chemical vapor deposition.17 Layer thicknesses were around 100–200 nm. Absolute Ge and C concentration were determined by RBS and crystalline quality was verified by channeling for the as-grown Si$_{1-x-y}$Ge$_x$C$_y$ layers. Additional x-ray diffraction confirmed the crystallinity and the degree of strain of the samples. From RBS and XRD, we notice that not all Ge and C were substitutionally incorporated in the samples, as part of them remain interstitial.

Prior to oxidation, samples were cleaned in a H$_2$SO$_4$ : H$_2$O$_2$ bath followed by a dip in diluted HF and rinsed in deionized water. Following the cleaning, samples were kept in an N$_2$ atmosphere until undergoing dry oxidation. We have straightforwardly extended this cleaning procedure from silicon to Si$_{1-x-y}$Ge$_x$C$_y$ with satisfactory results elsewhere.18 Rapid thermal oxidation between 900–1000 °C was performed, as well as conventional dry oxidation at 900 °C for 35 min. Oxide thicknesses were around 15–25 nm.

Raman spectroscopy measurements were performed in backscattering geometry using a Jobin Yvon T64000 spectrometer fitted with a metalagraphic microscope. An argon laser with a 488 nm blue line was used for excitation at room temperature. FTIR spectra were measured with a BOMEM DA8 spectrometer, with a glowar infrared source, a KBr beamsplitter, and a Mercury-Cadmium-Tellurium (MCT) detector. The effective detection window ranged from 400 to 4000 cm$^{-1}$. Absorption spectra were monitored in normal incidence in order to characterize the oxide, structurally. Non-oxidized samples were used as references.

III. RESULTS AND DISCUSSIONS

A. As-grown layers

We first analyze by Raman spectroscopy the crystallinity and the degree of strain of the epitaxial growth of the layers presented in Table I. We find that $x<0.2$ samples are completely strained, whereas for higher concentrations of Ge ($x=0.4$) the layers are relaxed. In Fig. 1 we present a typical
Si_{0.54}Ge_{0.43}C_{0.03} spectrum. There are four Raman peaks clearly resolved. The one located at around 298 cm\(^{-1}\) corresponds to the Ge–Ge vibrational mode. This peak is strongly dependent on Ge concentration but for concentrations below \(x=0.1\) is poorly resolved. The peak centered at 415 cm\(^{-1}\) corresponds to the Si–Ge bond. There are two bands related to the Si–Si bond. The first corresponds to the unstrained bulk Si–Si bond, which is centered at 520 cm\(^{-1}\) and that we have taken as a reference in assessing peak shifts. The second one corresponds to the compressively strained Si in the epilayer and is shifted toward a lower frequency with respect to the 520 cm\(^{-1}\) band. The two smaller peaks centered at 428 and 447 cm\(^{-1}\) have been attributed to the Si–Ge ordering in the layer.\(^{19}\)

We study now the shifts in the different bands as a function of the carbon composition of the layers. The resulting Si–Si shifts for different Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) samples are depicted in Fig. 2. From this graph we point out two different behaviors. First, we notice a linear dependence with carbon concentration. Second, we observe a significant difference in the behaviors of the strained and relaxed sets. In the literature, these shifts have already been explained by the presence of carbon in the lattice confining the phonons.\(^{13}\)

The full width at half maximum (FWHM) of the Si–Si strained peak is also sensitive to carbon concentration, as is evident in Fig. 3 where a clear increase of the width of the peak corresponds to increasing \(y\) values. We suggest that this behavior is due to the lattice disorder induced by a random distribution of carbon, when the concentration exceeds 0.5%.

### B. The layer after the oxidation

We now analyze the effects of thermal oxidations on Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) samples, with the objective of further understanding layer degradation and segregation of Ge into the Si. We have performed oxidations at 1000 °C up to 20 min and at 900 °C for 35 min. In all cases we have assured that the oxide thickness is never more than one tenth of the as-grown epitaxial layer thickness. A typical set of spectra for Si\(_{0.7}\)Ge\(_{0.2}\)C\(_{0.015}\) is presented in Fig. 4, with the Ge–Ge, Si–Ge, and Si–Si bands, as described in the Introduction, clearly resolved.

The positions and the shapes of the three peaks change with the oxidation process. The most dramatic change is in the Si–Si peak, which splits into two peaks. In Fig. 5 we have subtracted the unstrained Si–Si reference band at 520 cm\(^{-1}\) in order to better appreciate the structure of the strained peak. We believe that the explanation for the Si–Si peak splitting is the segregation of Ge into the Si substrate, which we have already characterized by means of a study of the concentration as a function of depth from the oxidation front, and reported previously.\(^{18,20}\) This segregation forms an enriched Ge layer just below the oxidation front, giving rise to a multilayer structure. This multilayer is responsible for the splitting of the strained peak because a different Ge con-
centration in each layer leads to a different peak shift. To quantify the Ge accumulation in this enriched layer we can rewrite Eq. (1)

\[ k_{\text{Si-Si}}(x) = 520 \text{ cm}^{-1} - 68x + 210y - 830 e_0(x), \]  

(5)

where we have also included the term related to carbon following Rücker and Methfensel.\(^{21}\) We have demonstrated elsewhere that carbon leaves substitutional position when oxidized in these conditions (1000 °C or 35 min at 900 °C).\(^{22}\) Thus, this term will only contribute in as-grown samples. If we compare the Raman shifts of Fig. 5 for each peak, we can estimate the Ge segregation. The strained Si–Si peak remains in the 510 cm\(^{-1}\) while the splitted peak shifts toward 505–506 cm\(^{-1}\). This peak is due to strained Si–Si bond in a Ge richer region. Substituting these values in expression (5) we obtain that Ge concentration increases up to 26%. These results agree fairly well with Ge accumulation obtained after concentration depth profiles (shown in Fig. 6) for Si\(_{0.9-y}\)Ge\(_{y}\)C\(_y\) samples where we observe an accumula-
tion of 15% for 10 min at 1000 °C, although further measurements to establish a definitive correlation will be required.

In samples with \(x=0.2\) it is also possible to study the Si–Ge and the Ge–Ge bands. In Fig. 4, we observe that the Ge–Ge and Si–Ge bands are strongly asymmetric; their intensity increases with oxidation time while their FWHM decreases. In Fig. 6 we have plotted the shifts of the Si–Ge band as a function of oxidation time for samples with two different carbon concentrations. We observe how the shift toward higher frequencies increases with oxidation time. We attribute these correlations (intensity, FWHM, and shifts) to the multilayer formation as explained in the previous paragraph. The enrichment of Ge leads to a positive shift in agreement with Eqs. (2) and (3), and moreover, a larger Ge concentration leads to a signal enhancement.

We also observe that while the Si–Si peak shows a stronger dependence on the oxidation at 1000 °C, the Si–Ge and Ge–Ge peaks are more sensitive to the longer oxidations at 900 °C, as is observed from the peak positions in Figs. 4 and 7. This can also be explained in terms of the Ge accumulation below the oxidation front. The Ge distribution depends on the oxidation conditions.\(^{13,20}\) At lower temperatures (\(<950 \text{ °C}\)) and longer oxidation times, Ge can diffuse deeper into the epilayer so that the Ge segregation shows a low concentration increase in a deeper depth. For oxidation at higher temperature (\(>1000 \text{ °C}\)) for shorter times, Ge is accumulated just below the oxidation front, increasing the Ge concentration without diffusing into the epilayer. The Raman measurement is more sensitive to the long-range diffusion in the case of the Si–Ge and Ge–Ge bands while for the case of the Si–Si band, it is more sensitive to increasing Ge accumulation in a thinner layer at the oxidation front.

C. Oxides grown from different epitaxial layers

As we have mentioned in the Introduction, vibrational frequencies depend on different parameters, like oxide thickness, image charge effects, inhomogeneities in the film, and
compressive stress. Oxide thicknesses are of the order of 25 nm for all samples. Thus, vibrational frequencies will not depend on oxide thickness or image charge effects.\(^2\) Furthermore, as we have already reported strong dependences of oxide kinetics on stress,\(^2\) we now justify the FTIR shifts on the basis of oxide stress as a function of the epilayer composition.

We study the growth of the oxide on Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) with fixed \(x=0.2\) and different carbon concentrations, along with a silicon reference sample free of stress. The results show slight, but significant, differences in peak positions and shapes, depending on the sample concentration and the thermal cycle undertaken. To carry out an accurate comparison between the different samples we have studied the shifts in the position of the vibrational mode TO\(_3\) with respect to pure SiO\(_2\). It is currently accepted that shifts toward larger frequencies are related to more relaxed oxides.\(^1\) In Fig. 8(a), we plot the absorbance of the TO\(_3\) modes in oxides grown in different epilayers. We find a shift toward larger frequency, as seen in Fig. 8(b). This is an expected trend since thicker oxides relax through viscous flow.\(^2\) An unexpected observation is that the oxides grown in the alloy layers are more relaxed than those grown on bulk silicon, irrespective of thickness. We believe that this result agrees with the relative magnitude of strain in Si\(_{1-x-y}\)Ge\(_x\)C\(_y\). For these measurements, the Ge concentration is the same for all the samples \((x=0.2)\) whereas \(y\) is varied. Carbon compensates the compressive strain induced by Ge in the epilayer. We thus find that oxides grow more relaxed in epilayers with a compressive strain.\(^1\)

From Fig. 8(b) we also observe that oxides grown at 1000 °C are more relaxed than those grown at 900 °C for a longer time, regardless of the carbon concentration. These results are already reported for silicon and are justified by means of the viscous flow relaxation model.\(^2\)

**IV. CONCLUSIONS**

We have studied the influence of carbon on the vibrational bands of Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) with different \(x\) and \(y\). We have found that the peak shifts follow a linear relationship with substitutional C concentration. We have characterized the effects of high temperature oxidation on Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) epilayers. We have found that the Raman Si–Si band associated with strained Si in the epitaxial layer splits into two peaks during oxidation at 1000 °C. We have attributed this effect to the accumulation of Ge in a layer below the oxidation front. As a consequence, the Si–Si bond gets more strained due to the local increase of Ge. Thus, as the goal is to preserve the Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) epilayer during the thermal process and to avoid Ge segregation, oxidation at a lower temperature \((900 °C)\) for a longer time are more convenient. We have also demonstrated that with more carbon in the epilayer, the grown oxide is more relaxed. We have concluded that the strain generated during the oxidation, due to the mismatch between the oxide and the epilayer, is better accommodated in processes at high temperatures for short times.

In conclusion, the complexity of strained Si\(_{1-x-y}\)Ge\(_x\)C\(_y\) epilayer oxidation requires certain tradeoffs in the oxidation
conditions, as the more relaxed oxides are obtained at the highest temperatures (1000 °C), whereas the preservation of epilayer uniformity requires lower temperatures (900 °C).