



Diffusion and clustering of supersaturated carbon in SiGeC layers under oxidation

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Abstract

In this work we investigated the diffusion and clustering of supersaturated substitutional carbon in 200 nm thick SiGeC layers buried under a silicon cap layer of 40 nm. The samples were annealed in either inert (N₂) or oxidizing (O₂) ambients at 850 °C for times ranging from 2 to 10 h. The silicon self-interstitial (I) flux coming from the surface under oxidation enhances the C diffusion with respect to the N₂ annealed samples. In the early stages of the oxidation process, the loss of C from the SiGeC layer by diffusion across the layer/cap interface dominates. This phenomenon saturates after an initial period (2–4 h) which depends on the C concentration. This saturation is due to the formation and growth of C containing precipitates which are promoted by the I injection and act as a sink for mobile C atoms. The competition between clustering and diffusion is discussed for two different C concentrations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years strong efforts have been devoted to the investigation of the structural properties of SiGeC alloy, due to its potential use as a Si-based material with band gap [1] and lattice parameter

[2] tailoring properties. Recently, the role of C in Si and SiGe alloys as a Si self-interstitial (I) trap was evidenced by the reduction of boron equilibrium diffusion [3] and by the suppression of both B transient enhanced diffusion (TED) and B oxidation enhanced diffusion (OED) [4,5]. This stimulated a renewed interest in the use of SiGeC layers to control the diffusion of dopants in silicon devices.

Therefore, understanding the behavior of C in SiGeC/Si heterostructures under I supersaturation is of crucial importance. It is known that C diffusion is strongly enhanced by I supersaturation [6],

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as the silicon self-interstitials promote the formation of mobile C interstitial atoms via the kick-out or Frank–Turnbull mechanisms. Recently, a C-diffusion enhancement caused by interstitial injection was also observed in SiGeC alloys with high C concentration, above 10^{20} cm^{-3} [7]. Nevertheless, even in the absence of an external I injection (i.e. after inert thermal annealing), it has been reported that the C tends to precipitate and form silicon carbide clusters [8].

The control of the C behavior in Si-based materials under thermal treatments is therefore challenging for technological applications. In this work we report on the diffusion and clustering behavior of C in buried SiGeC layers under supersaturated I non-equilibrium conditions. The non-equilibrium conditions are caused by thermal oxidation of the silicon cap. We describe the presence of a complex competitive mechanism between C diffusion and C accumulation in clusters.

2. Experimental

Two nominally 200 nm thick $\text{Si}_{0.926}\text{Ge}_{0.07}\text{C}_{0.004}$ and $\text{Si}_{0.922}\text{Ge}_{0.07}\text{C}_{0.008}$ layers covered by a 40 nm Si-cap were grown over a 200 nm thick silicon buffer layer by rapid thermal chemical vapor deposition (RTCVD) at temperatures between 625 and 750

°C on a p-type Czochralski (100) silicon wafer. The samples were cut in several pieces and thermally treated in a furnace at 850 °C under O_2 or N_2 fluxes for times ranging from 2 to 10 h. Even if the samples resulted to be slightly not homogeneous in the layer thicknesses, Rutherford back-scattering spectrometry (RBS) allowed monitoring with high accuracy the oxide thickness of the samples, as the thicknesses of the remaining Si cap and of the SiGeC layer. The longest annealing time of 10 h allowed nearly complete consumption of the Si cap by oxidation, whether in none of the processed samples oxidation of the SiGeC layer occurred. The samples were then analyzed with secondary ions mass spectroscopy (SIMS), high resolution X-ray diffraction (HRXRD) and by transmission electron microscopy (TEM).

3. Results and discussion

Figs. 1(a) and (b) report the C profiles obtained with SIMS from the samples with the lower C concentration annealed in O_2 and in N_2 at 850 °C. A clear diffusion effect occurs in the first stages of the annealing, as demonstrated by the shift of the C interface in Fig. 1(a). Such non-fickian behavior of C diffusion (no C is detected in the Si cap and no broadening of the interface is observed) will be

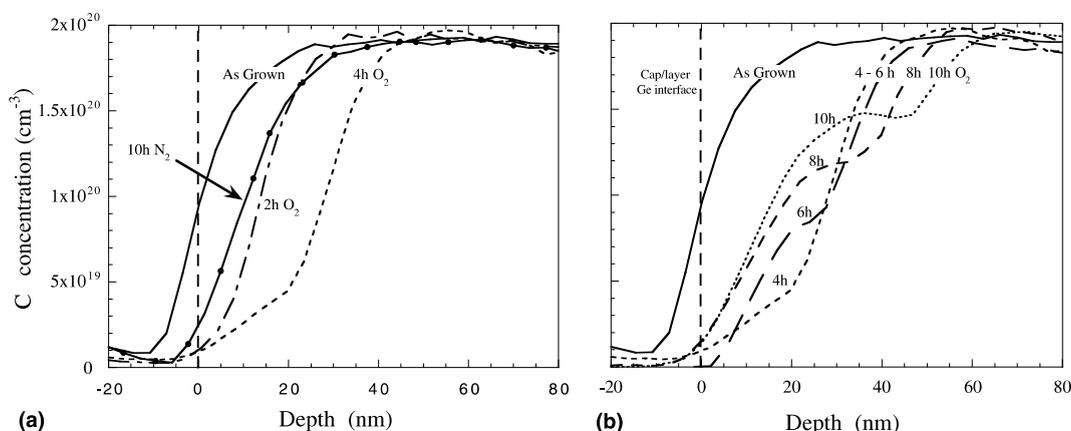


Fig. 1. Carbon concentration profile of the 0.35 at.% C samples relative to: (a) as grown (continuous line), 10 h annealed in inert atmosphere (marked by the arrow) and 2 and 4 h oxidation; (b) as grown (continuous line) and 4, 6, 8 and 10 h oxidation. The profiles were shifted in order to have the Ge cap/layer interface at depth zero, marked by the vertical dashed line.

explained in the following, during the discussion of the results. It is worth noting that SIMS analysis not reported here showed negligible Ge diffusion in all the processed samples either at the cap/layer and at the layer/substrate interfaces and no C diffusion occurs in the deeper part of the layer. This diffusion effect is much more remarkable in the O₂ annealed samples with respect to the N₂ samples, indicating that the I flux enhances the formation of mobile C, which can diffuse out from the layer.

The C profile evolution for annealing times longer than 4 h in O₂ (Fig. 1(b)) proceeds rather differently: as the annealing time increases the interface still moves deeper into the sample but, at the same time, an accumulation kink develops in the region between 20 and 45 nm in depth. Hence, a redistribution of C occurs inside the layer which, as we will show, is strictly related to a structural change of the material.

In Fig. 2 cross-section TEM image of the 0.35 at.% C sample annealed for 10 h in O₂ atmosphere is reported, where the formation of precipitates in the SiGeC layers is clearly visible. The precipitates, which do not form in the N₂ annealed samples, have a diameter of about 3–5 nm and are located between 20 and 120 nm in depth with a maximum density at a position where, according to the

SIMS, the C accumulates. XTEM after shorter annealing times (not reported) showed that both the total number of clusters and their maximum distribution depth increase with oxidation time. The TEM and SIMS results indicate that presumably the clusters contain C and act as a sink for the mobile C produced by the I injection.

HRXRD analyses confirm and give further insight to the above process. Fig. 3(a) reports the (004) rocking curve of the same sample of Fig. 2. Simulations of the rocking curves based on dynamical scattering theory were first attempted by using the C and Ge SIMS profiles and considering the Ge and C effect on strain as described in [2]. While this approach provided a successful fit of the as grown sample, on the contrary in the case of the oxidized samples we found no agreement between the experimental HRXRD data and the dynamical simulation (Fig. 3(a), dashed line). Therefore, after annealing in O₂ a certain amount of C is not on substitutional sites.

Hence, guided by the results showed in Figs. 1 and 2, we assumed that in the first 40 nm of the layer (kink zone) C is fully precipitated while in the region between 40 and 100 nm its substitutional fraction is varying linearly from 0 to 1, i.e. we assumed a substitutional-C profile following the solid line in Fig. 3(b). The agreement with the

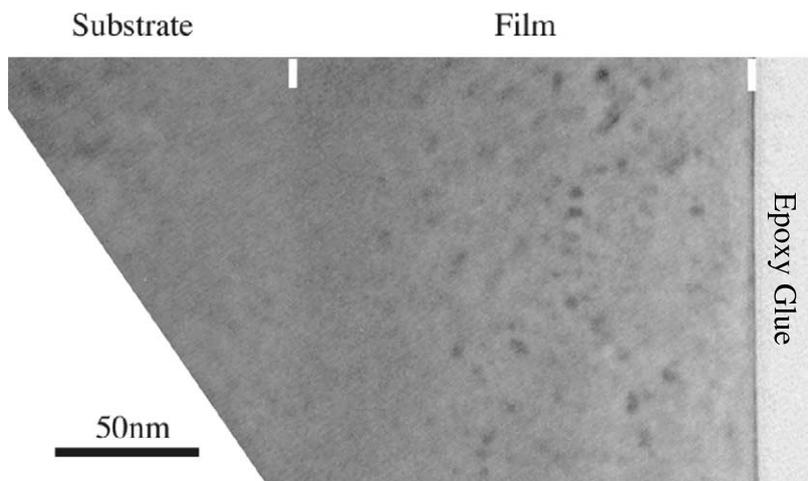


Fig. 2. TEM cross-section of the 0.35 at.% C sample annealed in O₂ atmosphere for 10 h. Three zones are visible in the picture. The left zone corresponds to the substrate, the central zone corresponds to the layer while the white right zone corresponds to the glue. The cap is not visible because almost completely oxidized and then removed by HF treatment. The precipitates are distributed inside the layer.

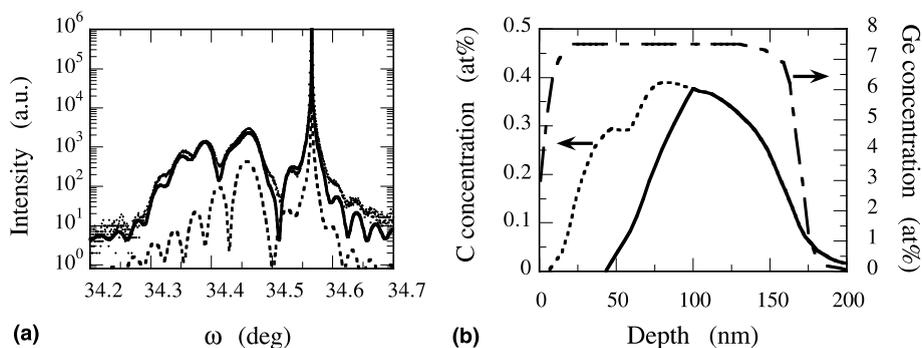


Fig. 3. (a) HRXRD (004) rocking curve of 0.35 at.% C 10 h oxidized sample (dots) compared to different simulations. (b) Concentration profiles used for the simulations. The Ge SIMS profile (dot-dashed line) was used for both the simulations. The C SIMS profile (dashed line) was used for the dashed line simulation in (a), assuming C and Ge to be fully substitutional. Solid line is the substitutional C profile used to generate the continuous line simulation in (a).

experimental data is now satisfactory (solid line in Fig. 3(a)), demonstrating conclusively the presence of an extended region of non-substitutional C atoms, which is qualitatively following the cluster distribution revealed by TEM.

The surface injection of I produces a significant structural change of the SiGeC layer, starting from the cap/layer interface and proceeding towards higher depths with the annealing time, involving a thickness of about 100 nm after 10 h in O₂ for a C concentration of 0.35 at.%. It is proposed that the main physical processes producing this structural modification are caused by C diffusion and precipitation.

Further insights are given by the experiments on samples with higher C concentration. Fig. 4 reports the C loss from the layer as a function of annealing time and for different C concentrations, compared to the I injected in the layer computed as in [9]. During the early stages of the oxidation, the amount of C lost by diffusion is, for both the investigated C concentrations, comparable to the number of I injected. This is similar to what observed in thinner samples of similar C concentration [7], where the complete loss of C from the layer was eventually observed. Our thicker samples behave differently, showing instead only a partial loss of C atoms which saturates after an initial transient. According to Fig. 4, the saturation dose appears to decrease with increasing the C concentration.

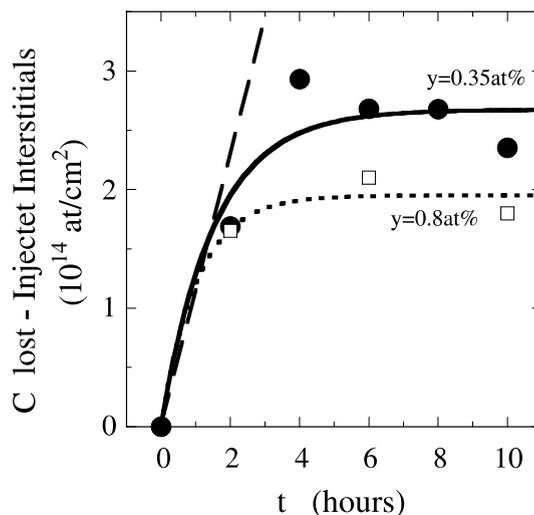


Fig. 4. C dose lost by the layer due to the oxidation process as a function of the annealing time. The C loss is evaluated by calculating the difference between the N₂ annealed and the O₂ annealed C dose. Data of both 0.35 at.% C series (full circles) and 0.8 at.% C series (open squares) are reported. The dashed line represents the I-injected during the thermal oxidation. Saturating exponential fits are reported to guide the eye.

The saturation of the C loss can be understood on the basis on the observed clustering phenomenon. The mobile C atoms promoted by the I injection can presumably diffuse both inside the layer and towards the surface. During the first stages of the annealing, the C atoms moving towards the surface have an increased mobility, as they are

moving inside a region which is both rich in I [9] and poor in traps (as C itself is a trap for mobile C) and therefore can easily leave the film through the cap. This explains also why no C is detected in the Si cap. The C which is diffusing through the cap is probably so fast that the concentration there falls below the SIMS detection limit.

Instead, C atoms moving inside the layer can start nucleating clusters by reacting with other C atoms. Moreover, following the calculations by Scholz et al. [10] of an interstitial undersaturation in the C-rich region, no mobile C would be produced inside the layer through the kick out reaction. As a consequence, the C at the interface which is made mobile by interaction with I and diffuses out, is not replaced by C atoms diffusing from inside (that would instead occur in the case of uniform C diffusivity). As a matter of fact, after 2 h of annealing the net result appears to be a simple shift of the cap/layer C interface instead of a fickian broadening.

After 4 h, a slight slope change in the bottom part of the interface shows the formation of the first clusters. These clusters are revealed by TEM in the first part of the layer. The growth of the kink from 4 to 10 h of annealing demonstrates that the clusters are able to capture the mobile C atoms moving towards the surface. The C loss saturates after 4 h, which suggests that at this stage of the process the cluster density is sufficiently high to trap the C diffusing atoms with 100% efficiency.

Following the above scenario, the fact that the saturation dose decreases with increasing C concentration may be interpreted as an increased clustering probability. The increase of the clustering probability would in fact cause a reduction of the diffusion effects, as confirmed by the fact that the saturation of the loss process is reached in a shorter time (see Fig. 4). The increase in clustering probability with the concentration is finally demonstrated by Fig. 5, where the cross-sectional TEM image of the 2 h O_2 annealed sample grown with a C concentration of 0.8 at.% is shown. As can be seen, small clusters form just below the cap/layer interface. No evidence of nucleation of such precipitates were instead observed in a sample with 0.35 at.% C after the same annealing of 2 h in O_2 .

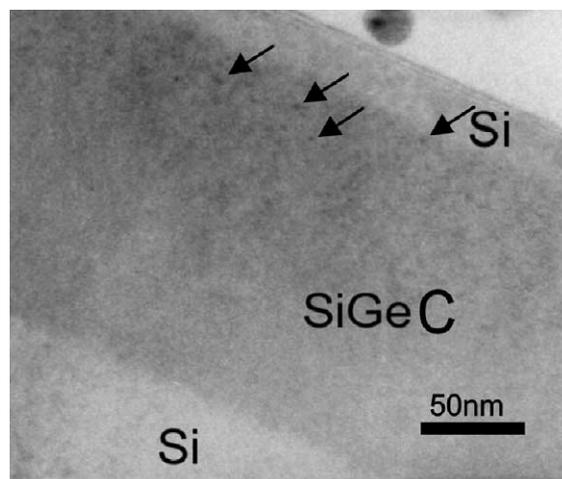


Fig. 5. Cross-sectional TEM image of the 0.8 at.% C sample annealed for 2 h in oxygen atmosphere. The arrows indicate the presence of small clusters just below the cap layer interface. Such clusters are not revealed in the equivalent sample with 0.35 at.% C composition.

4. Conclusions

Clear evidence of a competitive mechanism between C diffusion and clustering are reported in this work. In the early stages of oxidation, out-diffusion from the cap/layer dominates, whereas, when clustering begins to take place the C loss is progressively suppressed. Clusters are demonstrated to be fully efficient in trapping the mobile C after an initial transient of C out diffusion. The transient duration and the total amount of C loss depend on the C concentration. Indeed, we have demonstrated that for the higher C concentration, the clustering probability and efficiency in trapping mobile C is increased. According to the results presented in this work, both C clustering and diffusion may be controlled by varying the layer thickness and C concentration, beside the oxide grown thickness.

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References

- [1] K. Eberl, K. Brunner, O.G. Schmidt, in: R. Hull, J.C. Bean (Eds.), *Semiconductors and Semimetals*, Vol. 56, Academic Press, San Diego, 1999.
- [2] D. De Salvador, M. Petrovich, M. Berti, F. Romanato, E. Napolitani, A.V. Drigo, J. Stangl, S. Zerlauth, M. Mühlberger, F. Schäffler, G. Bauer, P.C. Kelires, *Phys. Rev. B* 61 (2000) 13005.
- [3] H. Rücker, B. Heinemann, W. Röpke, R. Kurps, D. Krüger, G. Lippert, H.J. Osten, *Appl. Phys. Lett.* 73 (1998) 1682.
- [4] P.A. Stolk, D.J. Eaglesham, H.J. Gossmann, J.M. Poate, *Appl. Phys. Lett.* 66 (1995) 1370.
- [5] M.S. Carrol, C.L. Chang, J.C. Sturm, T. Büyüklımanlı, *Appl. Phys. Lett.* 73 (1998) 3695.
- [6] U. Gösele, P. Laveant, R. Scholz, N. Engler, P. Werner, *Mater. Res. Soc. Symp. Proc.* 610 (2000) B7.1.1.
- [7] M.S. Carrol, J.C. Sturm, D. De Salvador, E. Napolitani, M. Berti, J. Stangl, G. Bauer, *Mater. Res. Soc. Symp. Proc.* 669 (2001) J6.7.
- [8] J.W. Strane, H.J. Stein, S.R. Lee, S.T. Picraux, J.K. Watanabe, J.W. Mayer, *J. Appl. Phys.* 76 (1994) 3656; A.R. Powell, F.K. LeGoues, S.S. Iyer, *Appl. Phys. Lett.* 64 (1994) 324; G.G. Fischer, P. Zaumseil, E. Bugiel, H.J. Osten, *J. Appl. Phys.* 77 (1995) 1934; L.V. Kulik, D.A. Hits, M.W. Dashiell, J. Kolodzey, *Appl. Phys. Lett.* 72 (1998) 1972.
- [9] M.S. Carrol, J.C. Sturm, *Mater. Res. Soc. Symp. Proc.* 610 (2000) B4.10.1.
- [10] R. Scholz, U. Gösele, J.Y. Huh, T.Y. Tan, *Appl. Phys. Lett.* 72 (1998) 200.