Symposium J, April, 2001, San Francisco, CA

Mat. Res. Soc. Symp. Proc. Vol. 669 © 2001 Materials Research Society

Carbon Diffusion and Clustering in SiGeC Layers Under Thermal Oxidation

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ABSTRACT

In this work we investigated the diffusion and clustering of supersaturated substitutional carbon 200nm thick SiGeC layers buried under a silicon cap layer of 40nm. The samples were annealed in inert (N_2) or oxidizing (O_2) ambient at 850°C for times ranging from 2 to 10 hours. The silicon self-interstitial (I) flux coming from the surface under oxidation enhances the C diffusion with respect to the N_2 annealed samples. In the early stages of the oxidation process, carbon escape by diffusion across the layer/cap interface dominates. This phenomenon saturates after an initial period (2-4h) 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.

INTRODUCTION

In the last 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 diffusion [3] and by the suppression of both B transient enhanced diffusion (TED) and B oxidation enhanced diffusion (OED) [4,5]. This pushed up 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], 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 by interstitials injection was observed also 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 the tendency of C to precipitate and to form β-SiC clusters [8].

All these facts suggest that the control of the C behavior in Si-based materials under thermal treatments is 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, induced by thermal oxidation of the silicon cap. We'll describe the presence of a complex competitive mechanism between C diffusion and C accumulation in clusters.

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EXPERIMENT

Two nominally 200nm thick $Si_{0.926}Ge_{0.07}C_{0.004}$ and $Si_{0.922}Ge_{0.07}C_{0.008}$ layers covered by a 40nm Si-cap were grown over a 200nm thick silicon buffer layer by rapid thermal chemical vapor deposition (RTCVD) at temperatures between 625°C and 750°C on a p-type Czochralski (100) silicon wafer. The samples were cut in several pieces that were thermally treated in furnace at 850°C under O_2 or N_2 fluxes for time from 2 to 10 hours. The N_2 annealing experiments were performed in order to distinguish the pure thermal effects from those produced by the I injection under oxidation.

The C and Ge chemical concentration depth profiles were obtained by Secondary Ions Mass Spectroscopy (SIMS) on a CAMECA IMS-4f spectrometer, while using Cs^+ or O_2^+ primary beam at impact energy below 2 keV and at glancing incidence, in order to improve the depth resolution. The C concentration was calibrated using the C total dose obtained by means of resonant Backscattering Spectrometry (rBS) technique [9], while the depth scale was calibrated by measuring the crater depth with a profilometer. High Resolution X-Ray Diffraction (HRXRD) measurements were performed by a Philips MRD diffractometer in standard setup (Ge(220) Bartels monochromator); (004) rocking curves were taken using a detector aperture of about 0.5 degrees.

RESULTS AND DISCUSSION

Fig. 1a and 1b report the C profiles of all the samples annealed in O_2, and of the sample annealed for 10 h in N_2. In order to consistently compare the profiles all the depth scales where shifted so as to have the Ge cap/layer interface at the same position, which has been conventionally assumed to be at zero (dashed vertical line in Fig. 1). In fact, after annealing, the cap/layer interface of the Ge signal results to be at different depths due to the volume expansion produced by the silicon cap oxidation. It is worth noting that SIMS analysis (not shown) reported negligible Ge diffusion in all the processed samples either at the cap/layer and at the

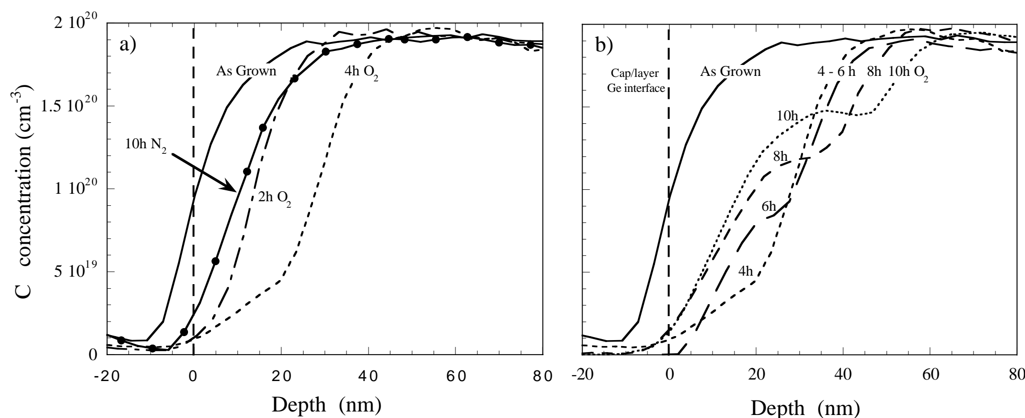

Figure 1 *Carbon concentration profile of the0.35at% C samples relative to: (a) as grown (continuous line), 10 hours annealed in inert atmosphere (marked by the arrow) and 2h and 4h oxidation; (b) as grown (continuous line), and 4h, 6h, 8h, and 10 h oxidation . The vertical line marks the presence of the Ge cap/layer interface.*

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layer/substrate interfaces. Moreover, the C diffusion is limited to the portion of the layer closer to the silicon cap, whether no diffusion occurs at the deeper interface. This is the reason why Fig. 1 reports only the region close to the cap/layer interface.

By comparing the C concentration profiles of the processed samples with that of the as grown (Fig.1a) a clear diffusion effect is evidenced by a shift of the C interface with respect to that of Ge. This effect is much more remarkable in the O_2 annealed samples with respect to the N_2 samples. The I flux evidently enhances the formation of mobile C which can diffuse out from the layer. The C profile evolution for annealing times longer than 4h in O_2 (Fig. 1b) is the following: the interface moves deeper into the sample as the annealing time increases and, at the same time, an accumulation kink grows up in the region between 20 and 45nm in depth.

The C diffusion is not the single mechanism induced in the layer by the I flux. In Fig.2 a cross sectional TEM image of the 0.35 at% C sample annealed for 10h in O_2 atmosphere is reported. The formation of precipitates in the SiGeC layers is clearly visible. Such precipitates have a diameter of about 3–5nm and are not revealed in the N_2 annealed samples. The clusters are not homogeneously distributed in the layer being located between 20 and 120nm in depth with a maximum density at the same depth as the accumulation kink of the C profile. XTEM on other samples (not reported) shows that both the total number of clusters and their maximum distribution depth increase with oxidation time. Such observations indicate a strong correlation between the clusters location and the C accumulation kink present in the SIMS profiles, suggesting that 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. 3a reports the (004) rocking curve of the sample annealed for 10 h in O_2.Simulations of the rocking curves based on dynamical scattering theory were attempted by using the C and Ge SIMS profiles, and considering the Ge and C effect on strain as described in Ref.[2].

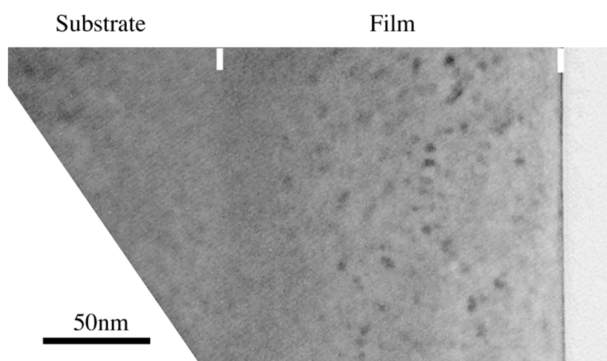

Figure 2 *TEM cross section of the 0.35at% C sample annealed in O_2 atmosphere for 10 hours. Three zones are visible in the picture. The left zone corresponds to the substrate, the central zone corresponds to the layer while the white right zone corresponds to the glue. The cap is not visible because almost completely oxidized and then removed by HF treatment. The precipitates are distributed inside the layer.*

While this approach provides a successful fit of the as grown sample, in the case of the oxidized samples, there is no agreement between the experimental HRXRD data and the dynamical simulations (Fig.3a, dashed line). However, the SIMS and TEM data suggest that not all the C atoms present in the layer are in substitutional sites and hence producing strain, but part of the C atoms is contained in the precipitates. We suppose that in the first 40nm of the layer (kink zone) C is fully precipitated while in the region between 40 and 100nm its substitutional fraction varies linearly from 0 to 1. The resulting substitutional-C profile is shown in Fig.3b as the solid line. This profile allows to produce the rocking curve reported in Fig.3a (solid line). The good agreement with the experimental data conclusively

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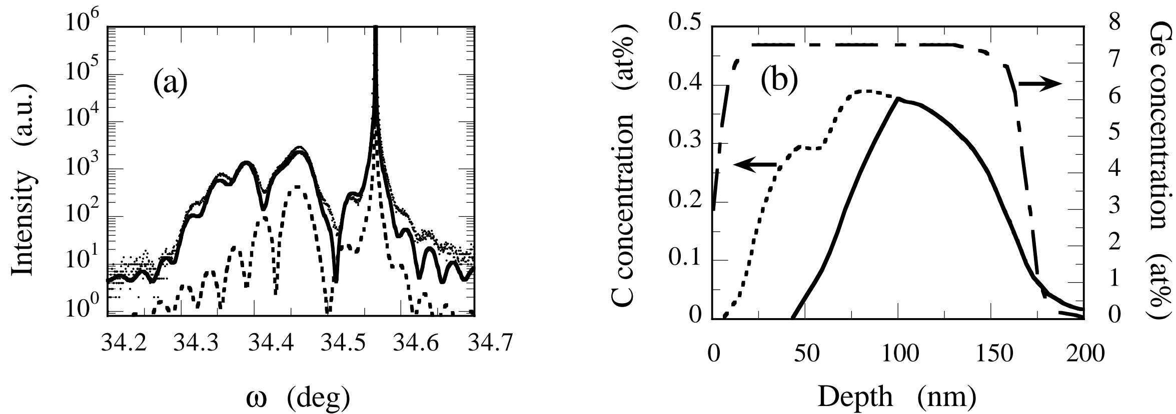

Figure 3 *(a) HRXRD (004) rocking curve of 0.35at% C 10 h oxidized sample (dots) compared to different simulations. (b) Concentration profiles used for the simulations. The Ge SIMS profile (dot-dashed line) was used for both the simulations. The C SIMS profile (dashed line) was used for the dashed line 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).*

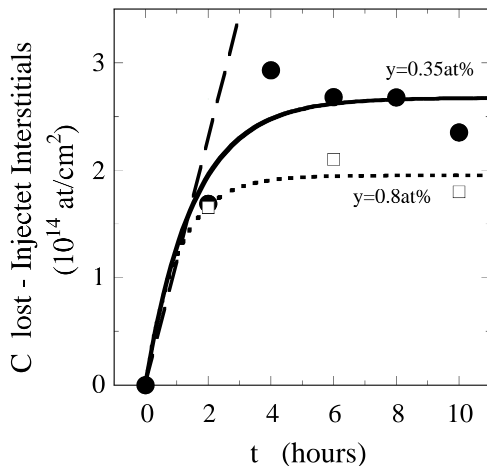

Figure 4 *C dose lost by the layer due to the oxidation process as a function of the annealing time. The C loss is evaluated by making the difference between the N_2 annealed and the O_2 annealed C dose. Data of both 0.35at% C series (full circles) and 0.8at% C series (open squares) are reported. The dashed line represents the I-injected during the thermal oxidation. Saturating exponential fits are reported to guide the eye.*

demonstrates the presence of a large zone of non substitutional C atoms in coincidence with the clusters revealed by TEM.

All the experimental observations indicate that the surface injection of I produces a strong structural change of the SiGeC layer. The change proceed with the annealing time from the cap/layer interface and involves about 100nm of the layer after 10h of annealing in O_2 when the C concentration is of 0.35at%. The main physical processes causing the structural modifications are C diffusion and precipitation.

During the early stages of the oxidation, the amount of C lost by diffusion is comparable to the I injected in the layer computed as in Ref.[10] (dashed straight line in Fig.4). This is similar to what observed in thinner samples of identical C concentration [7], where the complete loss of C from the layer was observed. On the contrary, in our samples there is only a partial loss of C atoms which saturates after an initial transient.

The saturation of the C loss can be understood on the basis of the observed clustering phenomenon. It is quite reasonable that the mobile C atoms promoted by the I injection can diffuse both inside the layer and towards the surface. During the first stages of the annealing, the C atoms moving towards the surface

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have an increased mobility, because they move inside a region which is both richer in I [10] and poorer in traps (as C itself is a trap for mobile C), so they can easily leave the film through the cap. Instead, C atoms moving inside the layer can start nucleating clusters by reacting with other C atoms. As a matter of fact, while after 2h of annealing the net result appears to be a simple shift of the cap/layer C interface, after 4h 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 assesses that the clusters are able to capture the mobile C atoms moving towards the surface. The C loss saturation observed after 4 hours demonstrated that at this stage of the process the cluster density is sufficiently high to trap all C atoms diffusing from the layer.

It is quite reasonable that the clustering and diffusion processes will change by changing the C concentration. Results concerning the 0.8at% C samples confirm this guess. The clustering probability is higher with respect to the low C concentration case as demonstrated by the cross sectional TEM image of the 2h O_2 annealed sample in Fig.5. As can be seen, small clusters just below the cap/layer interface appear. On the contrary, no evidence of nucleation of such precipitates is visible in the equivalent samples with 0.35at% C (not shown). The increase of the clustering probability causes a reduction of the diffusion effects. As a matter of fact, the total amount of C lost by the layer is lower at higher concentration and the saturation of the loss process is reached in a shorter time (see Fig.4). Furthermore, the redistribution of C inside the layer is also reduced being the evolution of an accumulation kink not present in the SIMS analyses (not shown) as in the case of low C content. In other words the clusters efficiency in trapping the mobile C increases with the concentration or equivalently the mean free-path of mobile C before being trapped decreases.

CONCLUSIONS

In this work the evolution of structural properties of SiGeC layers buried under a Si cap under oxidation was investigated. Clear evidences of both C diffusion and clustering are reported. It is experimentally demonstrated that the oxidation-induced I flux strongly enhances both

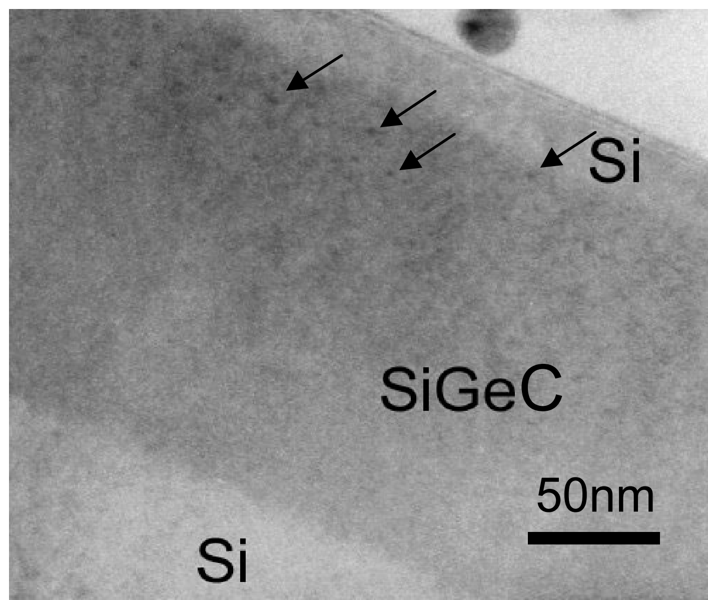

Figure 5 *Cross sectional TEM image of the 0.8at% C sample annealed for 2 hours in oxygen atmosphere. The arrows indicate the presence of small clusters just bellow the cap layer interface. Such clusters are not revealed in the equivalent sample with 0.35at% C composition.*

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phenomena with respect to the annealing in inert atmosphere. A strong competition between the diffusion and clustering processes is observed. 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 full 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 the higher is the C concentration the higher is the clustering probability and efficiency in trapping mobile C.

ACKNOWLEDGEMENTS

The authors wish to thank C. Spinella and S. Pannitteri for TEM analyses. This work was partially supported by SIGENET, the EC program for improving Human Potential-Research Training Network, Contract No. HPRN-CT-2000-00123.

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