SiGeC alloy layer formation by high-dose C^+ implantations into pseudomorphic metastable $Ge_{0.08}Si_{0.92}$ on Si(100)

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Dual-energy carbon implantation ($1\times10^{16}/cm^2$ at 150 and at 220 keV) was performed on 260-nm-thick undoped metastable pseudomorphic Si(100)/ $Ge_{0.08}Si_{0.92}$ with a 450-nm-thick SiO_2 capping layer, at either room temperature or at 100 °C. After removal of the SiO_2 the samples were measured using backscattering/channeling spectrometry and double-crystal x-ray diffractometry. A 150-nm-thick amorphous layer was observed in the room temperature implanted samples. This layer was found to have regrown epitaxially after sequential annealing at 550 °C for 2 h plus at 700 °C for 30 min. Following this anneal, tensile strain, believed to result from a large fraction of substitutional carbon in the regrown layer, was observed. Compressive strain, that presumably arises from the damaged but nonamorphized portion of the GeSi layer, was also observed. This strain was not significantly affected by the annealing treatment. For the samples implanted at 100 °C, in which case no amorphous layer was produced, only compressive strain was observed. For samples implanted at both room temperature and 100 °C, the channelled backscattering yield from the Si substrate was the same as that of the virgin sample. *© 1997 American Institute of Physics.* [S0021-8979(97)00704-4]

I. INTRODUCTION

Strained pseudomorphic Ge_xSi_{1-x} alloy layers have been extensively studied due to such properties as adjustable band gap and their potential applications to optical and electrical devices such as infrared detectors, heterojunction bipolar transistors, modulation doped field effect transistors, and Schottky collector heterojunction bipolar transistors.[1–4] Recently, for the same potential benefits, $Si_{1-x-y}Ge_xC_y$ alloy layers have been epitaxially grown by molecular-beam epitaxy,[5,6] chemical-vapor deposition,[7,8] or by solid-phase epitaxial annealing following high-dose implantation.[9,10] Valence band offset or conduction band offset in the SiGeC layers has also been investigated and reported.[11] $Si_{1-x-y}Ge_xC_y$ alloy layers have shown less compressive strain than Ge_xSi_{1-x} alloy layers due to the strain compensation or shown rather tensile strain depending on the C and Ge composition in the layers.[5–8] Because the main effect of substitutionally incorporated carbon in the strained GeSi layers is strain compensation, it is expected that thick SiGeC layers can be grown without generation of misfit or threading dislocations. However, the complete substitutionality of C is not easy to achieve in all methods of epitaxial growth due to the low solubility of C in Si, and the tendency of carbon to form silicon carbide, or C–C bonds.[8] If the carbon is not in substitutional sites, the potential band gap and strain compensation effects may not be obtained. In the present study, we report the substitutionality of C in $Si_{1-x-y}Ge_xC_y$ alloy layers obtained by high-dose carbon implantation into a molecular-beam-epitaxy grown GeSi layer, and also report the effects of nonsubstitutional carbon on the structural properties of GeSi alloy layers.

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II. EXPERIMENTS

Undoped $Ge_{0.08}Si_{0.92}$ alloy layers were epitaxially grown on undoped Si(100) substrates in a molecular-beam-epitaxy chamber. The thickness of the layer was about 260 ± 10 nm as measured by MeV ^4He backscattering spectrometry. The as-grown samples were of excellent crystalline quality, with a minimum channeling yield of ~3.5% (Fig. 2). The (400) double-crystal x-ray diffractometry on the as-grown $Ge_{0.08}Si_{0.92}$ shows a peak at a relative angle of −0.227° using Cu $K\alpha$ radiation ($\lambda=1.54$ Å) (Fig. 3). This value corresponds to a perpendicular strain of 0.57% and is consistent with the strain expected in a pseudomorphic metastable $Ge_{0.08}Si_{0.92}$ layer on Si(100), based on elastic deformation theory. A 450-nm-thick SiO_2 layer was deposited on the as-grown $Ge_{0.08}Si_{0.92}$ layer by chemical-vapor deposition at 300 °C. This SiO_2 cap was added to absorb some of the energy of the carbon ions and restrict their projected range to the epitaxial GeSi layer. Double-energy carbon implantation ($1\times10^{16}/cm^2$ at 150 and at 220 keV) into this layer structure at either room temperature (RT) or at 100 °C was employed to obtain an approximately uniform carbon profile. A simulated (TRIM-92) C depth profile shows fair agreement with the C profiles obtained from the implanted samples by secondary ion mass spectrometry (SIMS) (see Fig. 1). The SiO_2 capping layer was then removed by etching using a 3% dilute HF solution. All the implanted samples were subjected to steady-state annealing in a vacuum ambient of 5×10^{-7} Torr at 550 and 700 °C. The depth profile of the implanted carbon was determined by using SIMS. The damage and strain of the implanted $Ge_{0.08}Si_{0.92}$ layers before and after annealing were characterized by 2.0 MeV $^4He^{++}$ backscattering/channeling spectrometry and by symmetrical (400) x-ray rocking curves taken with a double-crystal x-ray diffractometer. Raman spectroscopy using an Ar laser of a

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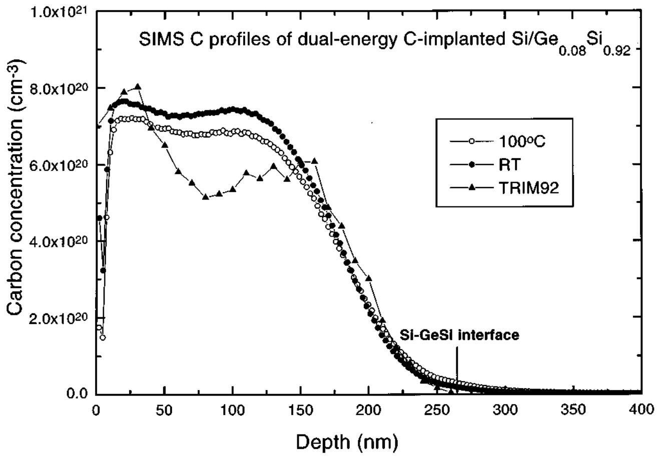

FIG. 1. Carbon depth profiles obtained by secondary ion mass spectrometry from carbon ($1 \times 10^{16}/cm^2$ at 150 keV plus $1 \times 10^{16}/cm^2$ at 220 keV) implantation into GeSi layers at either room temperature or at 100 °C. The profile simulation obtained using TRIM-92 is also shown. The Si/GeSi interface is indicated by an arrow.

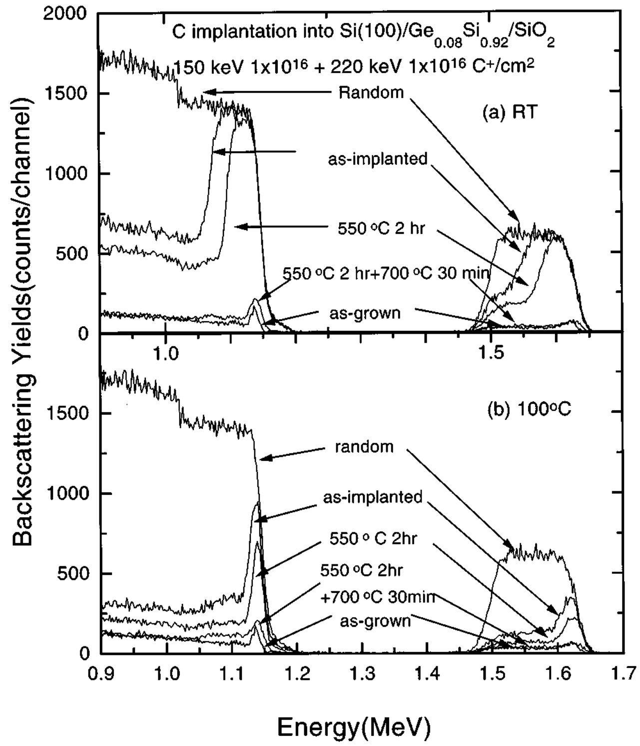

FIG. 2. The 2.0 MeV ^{4}He ⟨100⟩ channeling spectra for metastable pseudomorphic $Ge_{0.08}Si_{0.92}$ layer grown on Si(100) implanted with $1 \times 10^{16}/cm^2$ 150 keV C ions and $1 \times 10^{16}/cm^2$ 220 keV C ions: (a) at room temperature, and (b) at 100 °C. A thickness of 150 nm is amorphized by this double-energy implantation and solid-phase regrowth is completed by a sequential anneal at 550 °C for 2 h and 700 °C for 30 min. The channeling and random spectra of a virgin sample are also shown in both figures as references.

wavelength, 488 nm, was performed at room temperature to observe the local vibration mode (LVM) of substitutional C atoms on the Si site.

II. RESULTS AND DISCUSSION

Figure 1 shows carbon depth profiles which have been determined by secondary ion mass spectrometry after double-energy implantation at room temperature or at 100 °C. The profiles of the two samples are similar and exhibit a fairly uniform concentration from about 50 to 120 nm. At the latter depth, the concentration of carbon is estimated at about 7×10^{20} cm^{-3} (1.4 at. %). Since the Ge concentration is 8%, the carbon concentration is estimated to exceed a concentration required to compensate the inherent compressive strain in as-grown $Ge_{0.08}Si_{0.92}$. According the Vegard's law, the Ge/C ratio for perfect strain compensation is about 10.8 while the ratio in the present study is about 5.7. This may convert the strain state from compressive to tensile in the GeSi film.[5–9]

Backscattering/channeling spectra for implanted samples, after implantation at room temperature and after annealing, are shown in Fig. 2(a). The data in this figure indicate that an amorphous layer (thickness about 150 nm) was present after implantation. Annealing at 550 °C for 2 h resulted in partial regrowth of the amorphous layer and a subsequent anneal at 700 °C for 30 min resulted in complete regrowth of the layer. The channeling yield from the sample after the final anneal is slightly higher than for the as-grown sample both within the previously amorphized region and near the amorphous/crystalline interface, while the yield behind the implanted layer is the same as that in the as-grown sample. The corresponding spectra for samples implanted at 100 °C are presented in Fig. 2(b). In this case, an amorphous layer was not formed, although there was significant damage near the surface of the sample. This may be because of dynamic annealing, which is mainly the recombination of recoiled interstitials with vacancies created during implantation.[12,13] After the completion of the same two-step annealing cycle employed for the samples implanted at room temperature, the channeling yield from the initially damaged region of the sample is slightly higher than that for the as-grown sample, while the yield arising from greater depths is the same as for the as-grown sample.

Double-crystal rocking curves obtained from samples implanted at room temperature and from a virgin GeSi sample are shown in Fig. 3(a). A tensile strain as well as a compressive strain is observed for the layer, which exhibited full solid-phase epitaxial regrowth, whereas the as-grown layer shows only normal strain relaxation after an identical thermal process. The spectrum for the sample annealed at 550 °C for 2 h and at 700 °C for 30 min shows a compressive strain peak (near −0.227°) in almost the same position and intensity as shown in the as-implanted layer. Rocking curves for 100 °C-implanted samples are shown in Fig. 3(b). In this case, there is no evidence of tensile strain after the same two cycle anneal sequence. Instead, the rocking curve remains basically unchanged upon annealing.

Raman spectra are shown in Fig. 4 for an unimplanted sample and for annealed samples which were implanted at room temperature or at 100 °C. The spectrum for the room-temperature-implanted sample exhibits the well-known local vibrational mode of substitutional C in Si at a wave number of 610 cm^{-1}. However, both the as-grown and the 100 °C-implanted samples show no sign of carbon substitutionality

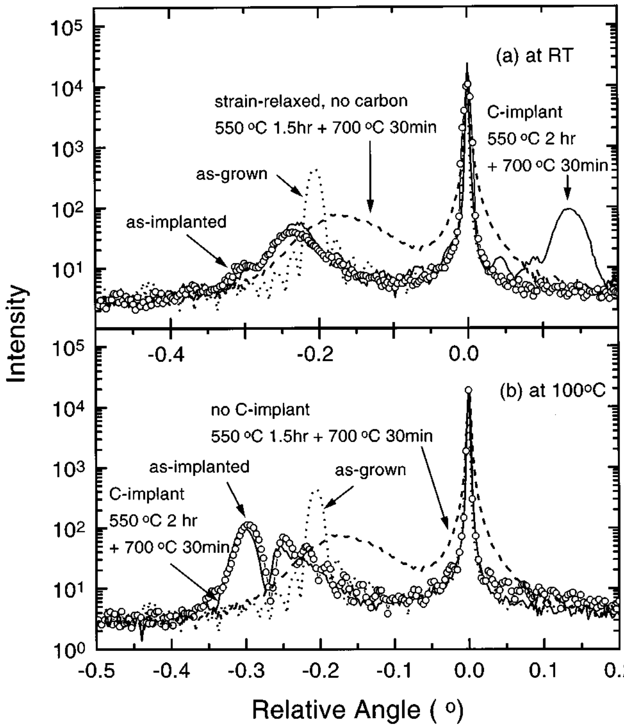

FIG. 3. Double-crystal rocking curves of (400) symmetrical diffraction taken with Cu $K\alpha$ radiation ($\lambda=1.54$ Å) for a metastable pseudormorphic $Ge_{0.08}Si_{0.92}$ layer grown on Si(100) implanted with $1\times10^{16}/cm^2$ 150 keV C ions and $1\times10^{16}/cm^2$ 220 keV C ions: (a) at room temperature, and (b) at 100 °C. Rocking curve spectra of virgin samples (as-grown, and strain-relaxed) are also shown in both figures as references.

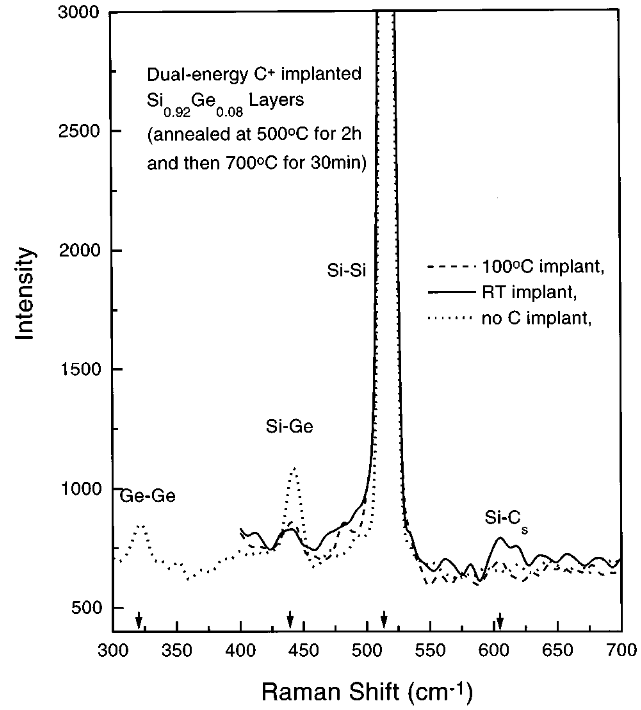

FIG. 4. Raman spectra measured for the SiGeC samples after double-energy implantation (at room temperature and at 100 °C) and sequential annealing at 550 °C for 2 h and at 700 °C for 30 min. The spectrum from the as-grown GeSi is included as a reference. The local vibration mode of C in Si at 610 cm^{-1} is only observed from the sample implanted at room temperature.

at the same wave number. In addition, no indication of the local vibration by SiC precipitates ($\sim$800 cm^{-1}) was found in either of the SiGeC layers formed by the implantation of carbon. (Figure does not show the range of wave number.)

We suggest the following explanation for the observations presented above. The carbon in the initially amorphous portion of the sample implanted at room temperature is largely substitutional following regrowth leading to the tensile strain peak in Fig. 3(a). (The solid-phase epitaxy of SiGeC alloys usually results in substitutionality of the carbon atoms.[9]) The carbon in the nonamorphized portion of the room-temperature-implanted samples remains nonsubstitutional following the anneal sequence. These carbon atoms may form complexes or act as sinks which hold recoiled silicon interstitial atoms, consistent with the observations of Tamura *et al.*[14] The stabilization of the silicon interstitials by nonsubstitutional carbon then leads to the insignificant effect of annealing on the compressive strain introduced during implantation in the nonamorphized region. The channeling yield in Fig. 2(a) after the full regrowth of the amorphous layer differs insignificantly from that of the as-grown sample over the whole range of the Ge signal, but is slightly enhanced in the Si signal of the corresponding region (1.05–1.15 MeV). This observation suggests that the nonsubstitutional fraction of the carbon stabilizes Si interstitials only. We also note that the channeling yield that emanates from the Si substrate recovers fully to the value for the virgin sample. This is in contrast to the results for regrown metastable pseudomorphic GeSi amorphized by As or P irradiations,[15,16] where the channeling yield from the Si substrate remains several times higher than that of the virgin sample after regrowth. This difference can be attributed to a relaxation of the strain in the GeSi upon regrowth for the As and P case, while such a relaxation does not occur here with C. The results for the 100 °C-implanted sample are similarly unaffected by annealing and can be explained in the same manner. In particular, there is an indication that the channeling yield in Fig. 2(b) of the Si signal near 1.11 MeV of the fully annealed sample slightly exceeds that of the corresponding Si signal in Fig. 2(a). That small difference is absent near 1.07 MeV. Although the magnitude of the difference is marginal, it is consistent with a higher concentration of interstitial silicon induced by nonsubstitutional carbon in the implanted region of the 100 °C-implanted sample than in the room-temperature-implanted sample.

The fraction of the carbon which is substitutional can be estimated by comparing the value of the carbon concentration obtained from the SIMS data (about 1.4%) with a value extracted from the observed position of the tensile strain peak at +0.135°, assuming that the tensilely strained GeSi is perfectly pseudomorphic without any strain relaxation. According to Vegard's law, a ratio of Ge to C of 10.8/1 is required for perfect strain compensation, i.e., to maintain the lattice constant of Si. A C concentration of 1.4% in a SiGeC layer with 8 at. % Ge thus decreases the lattice constant by −0.25%, which predicts that as a pseudomorphic layer this film will have a perpendicular tensile strain of 0.25 $(1+\nu)/$

$(1-\nu)\%=0.43\%$, where ν is 0.27 (Poisson's ratio of Si). This number corresponds to an angular peak position at $+0.17°$ in the rocking curve. Since the tensile strain observed in Fig. 3(a) generates a peak position of $+0.135°$ in the present sample, a substitutionality fraction of approximately $0.135/0.17=80\%$ is estimated. However, if the Ge/C ratio for perfect strain compensation is about 8.3, as proposed by some researchers,[6] the C substitutionality increases to about 90%.

It is appropriate to discuss the possible consequences of oxygen atoms which may recoil into the GeSi layer from the initial SiO_2 capping layer. According to the simulation by Christel *et al.*, the recoiled oxygen dose is less than 10% of the implanted carbon dose, and the concentration of the oxygen atoms exponentially decreases with the distance from the surface of an implanted sample.[17] It is possible that oxygen-induced defects or SiO_x particles form in the sample surface during the implantation and the annealing, which may account for some of the high backscattering yield observed after annealing as shown in Figs. 2(a) and 2(b). Even with the presence of this unwanted incorporation of oxygen atoms, all the effects observed above are presumed to result from implanted carbon atoms because it is clear that the content of carbon is much higher than that of oxygen in the GeSi layer.

IV. SUMMARY

Double-energy room-temperature implantation resulted in amorphization of the GeSi layer to a depth of 150 nm. At elevated temperatures, the amorphized layer was shown to epitaxially grow with tensile strain due to carbon overcompensating the preexisting compressive strain, since solid phase epitaxy leads to most of the carbon atoms (more than 80%) occupying substitutional sites. However, the nonamorphized portion of the layer preserved additional compressive perpendicular strain after C^+ irradiation damage, which was not removed by annealing, probably because carbon atoms in this nonamorphized layer sit in nonsubstitutional instead of substitutional sites. Similar results were found from the samples implanted at 100 °C. These films showed no amorphization due to the dynamic annealing effect and no tensile strain even after annealing at 700 °C for 30 min. The additional strain created by C^+ implantation damage was never removed by annealing.

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[1] T. L. Lin, A. Ksendzov, S. M. Dejewski, E. W. Jones, R. W. Fathauer, T. N. Krabach, and J. Maserjian, IEEE Trans. Electron Devices **ED-38**, 1141 (1991).
[2] S. S. Iyer, G. L. Patton, J. M. C. Stork, B. S. Meyerson, and D. L. Harame, IEEE Trans. Electron Devices **ED-36**, 2043 (1989).
[3] H. Daembkes, H.-J. Herzog, H. Jorke, H. Kibbel, and E. Kasper, IEEE Trans. Electron Devices **ED-33**, 633 (1986).
[4] O. Nur, M. Willander, H. H. Radamson, M. R. Sardela, Jr., G. V. Hansson, C. S. Petersson, and K. Maex, Appl. Phys. Lett. **64**, 440 (1994).
[5] H. J. Osten, E. Bugiel, and P. Zaumseil, Appl. Phys. Lett. **64**, 3440 (1994).
[6] K. Eberl, S. S. Iyer, S. Zollner, J. C. Tsang, and F. K. LeGoues, Appl. Phys. Lett. **60**, 3033 (1992).
[7] J. L. Regolini, F. Gisbert, G. Dolino, and P. Boucaud, Mater. Lett. **18**, 57 (1993).
[8] J. Mi, P. Warren, P. Letourneau, M. Judelewicz, M. Gailhanou, M. Dutoit, C. Dubois, and J. C. Dupuy, Appl. Phys. Lett. **67**, 259 (1995).
[9] J. W. Strane, H. J. Stein, S. R. Lee, B. L. Doyle, S. T. Picraux, and J. W. Mayer, Appl. Phys. Lett. **63**, 2786 (1993).
[10] S. Im, J. Washburn, G. Gronsky, N. W. Cheung, K. M. Yu, and J. W. Ager, Appl. Phys. Lett. **63**, 2682 (1993).
[11] F. Meyer, D. Bouchier, MRS symposium in San Francisco, Spring 1996 (unpublished).
[12] T. E. Haynes and O. W. Holland, Appl. Phys. Lett. **61**, 61 (1992).
[13] J. S. Williams, M. C. Ridgeway, R. G. Elliman, J. A. Davies, S. T. Johnson, and G. R. Palmer, Nucl. Instrum. Methods Phys. Res. B **55**, 602 (1991).
[14] M. Tamura, T. Ando, and K. Ohyu, Nucl. Instrum. Methods Phys. Res. B **59/60**, 572 (1991).
[15] D. Y. C. Lie, J. H. Song, F. Eisen, M.-A. Nicolet, and N. D. Theodore, J. Electron. Mater. **25**, 87 (1996).
[16] D. Y. C. Lie, S. Im, M.-A. Nicolet, and N. D. Theodore, J. Appl. Phys. **79**, 8341 (1996).
[17] L. A. Christel, J. F. Gibbons, and S. Mylroie, Nucl. Instrum. Methods **182/183**, 187 (1981).