Characterization of Si$_{1-x-y}$Ge$_x$C$_y$ films grown by C$^+$ implantation and subsequent pulsed laser annealing

Jian-Shing Luo$^a$, Wen-Tai Lin$^{a,*}$, C.Y. Chang$^b$, P.S. Shih$^b$, F.M. Pan$^c$, T.C. Chang$^c$

$^a$Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan
$^b$Department of Electronics Engineering, National Chiao Tung University, Hsinchu, Taiwan
$^c$National Nano Device Laboratory, Hsinchu, Taiwan

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Abstract

Epitaxial Si$_{1-x-y}$Ge$_x$C$_y$ films have been grown by C$^+$ implantation into Si$_{0.76}$Ge$_{0.24}$ films with a dose of $1.0 \times 10^{16}$/cm$^2$ and subsequent pulsed KrF laser annealing at an energy density of 0.3–1.6 J/cm$^2$. Upon laser annealing Ge segregation to the film surface and diffusion to the underlying Si appeared at energy densities above 0.8 J/cm$^2$ and 1.4 J/cm$^2$, respectively, while the depth profiles of C remained nearly unchanged as in the as-implanted Si$_{1-x-y}$Ge$_x$C$_y$ film. Concurrently, no SiC and twin were observed. The amount of C incorporated into substitutional sites initially increased with the energy density in the range of 0.3–1.0 J/cm$^2$, and then saturated at an energy density of 1.0–1.6 J/cm$^2$. For the Si$_{1-x-y}$Ge$_x$C$_y$ films grown at 1.0 J/cm$^2$ for 5 and 20 pulses SiC was formed with its amount increasing with the pulse number because of C segregation to the film surface and the original amorphous/crystal interface where the EOR defects were present. For the Si$_{1-x-y}$Ge$_x$C$_y$ films grown at energy densities below 1.0 J/cm$^2$ the reduction of tensile stress mainly resulted from the effect of substitutional carbon incorporation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Si$_{1-x}$Ge$_x$ films grown on Si have great potential for fabricating high-speed electronic and optoelectronic devices [1,2]. The band gap of Si$_{1-x}$Ge$_x$ films decreases monotonically with the Ge concentration. Carbon substitutionally introduced into Si$_{1-x}$Ge$_x$ films may change the band gap [3–5], providing an additional design parameter in band structure engineering on Si. In addition, the addition of C can also reduce the lattice mismatch between Si$_{1-x}$Ge$_x$ and Si, opening up the opportunities for fabricating thicker pseudomorphic Si$_{1-x}$Ge$_x$ films with a high Ge content. Recently, pseudomorphic Si$_{1-x-y}$Ge$_x$C$_y$ films with carbon concentrations in the range of 1–2 at.% have been grown by many methods such as molecular beam epitaxy [6,7], chemical vapor deposition [8,9], and solid phase epitaxy [10–12]. Since the maximum solubility of substitutional C in Si is much lower ($\sim 10^{-5}$) than that required for strain compensation, SiC phase may form in the Si$_{1-x-y}$Ge$_x$C$_y$ films during growth, especially at temperatures above 600°C [13]. Pulsed laser annealing is a promising technique for growing epitaxial thin films under nonthermal equilibrium conditions. By this method, above 1.0 at.% of substitutional C could be introduced into Si due to the fast melting and resolidification process [14–16]. Ion implantation is a technique highly compatible with the standard silicon process. As we know, few papers concerning the Si$_{1-x-y}$Ge$_x$C$_y$ films grown by ion implantation with subsequent pulsed laser annealing have been reported [16–19]. In the present work, we explore the effects of energy density and pulse number on the characterization of epitaxial Si$_{1-x-y}$Ge$_x$C$_y$ films grown by C$^+$ implantation into Si$_{0.76}$Ge$_{0.24}$ films followed by pulsed KrF laser annealing.

2. Experimental

Epitaxial Si$_{0.76}$Ge$_{0.24}$ films about 0.15 μm thick were grown on n-type (100)Si at 550°C by ultra-high vacuum chemical vapor deposition (CVD). The as-grown Si$_{0.76}$Ge$_{0.24}$ films were partially relaxed. C ions were implanted at an acceleration voltage of 80 keV with a dose of $1.0 \times 10^{16}$/cm$^2$. During implantation the temperature of the samples remained below 200°C. In order to confine most
of the implanted ions in the Si$_{0.76}$Ge$_{0.24}$ films, a SiO$_2$
overlayer about 1500 Å thick was grown on the as-grown
Si$_{0.76}$Ge$_{0.24}$ films. The maximum of the implanted profile in
the Si$_{0.76}$Ge$_{0.24}$ films was estimated to be ~900 Å by TRIM
simulation [20]. Before pulsed laser annealing the SiO$_2$
layer was chemically removed by 5% HF solution.

Pulsed KrF laser annealing was performed at an energy
density of 0.1–1.6 J/cm$^2$ in a vacuum around 2 × 10$^{-6}$ Torr.
The laser beam was focused onto an area of 4 × 4 mm$^2$. The
duration time was 14 ns. The repetition rate was 1 Hz. For
each annealing the sample was illuminated by one pulse
unless otherwise specified. The microstructure and chemical
compositions of Si$_{1-x-y}$Ge$_x$C$_y$ films were analyzed by
energy dispersive spectrometry (EDS)/transmission electron
microscope (TEM) which was equipped with a field
emission gun with an electron probe 12 Å in size. The
variation of the lattice constant of Si$_{1-x}$Ge$_x$C$_y$ films
was analyzed by X-ray diffraction (XRD) with Cu K$_\alpha$
radiation. The depth profile of C in the Si$_{1-x-y}$Ge$_x$C$_y$
films was examined by secondary ion mass spectrometry (SIMS).
Absorption measurements were performed on a Fourier
transform infrared spectrometer (FTIR). Samples with lar-
ged irradiated areas (10 × 10 mm$^2$) made of nine adjacent
4 × 4 mm$^2$ areas irradiated under identical conditions were
prepared for XRD, SIMS, and FTIR analyses.

3. Results and discussion

After C$^+$ implantation an amorphous layer about 900 Å
thick was formed on the Si$_{0.76}$Ge$_{0.24}$ film as shown in Fig. 1.
Upon subsequent laser annealing polycrystal Si$_{1-x-y}$Ge$_x$C$_y$
films were formed at 0.2 J/cm$^2$, while epitaxial
Si$_{1-x-y}$Ge$_x$C$_y$ films were formed at 0.3–1.6 J/cm$^2$ as shown
in Fig. 2, in which the end-of-range (EOR) defects are
present in the original amorphous/crystal interface. For laser
annealing of Si the melting depth is a function of the laser
wavelength, pulse length, energy density, and the thickness

![Fig. 1. XTEM image of the as-implanted Si$_{1-x-y}$Ge$_x$ film showing the
formation of an amorphous Si$_{1-x-y}$Ge$_x$C$_y$ layer.](image1)

of the amorphous Si layer [16,21,22]. In the present study
the melting depth at 0.3 J/cm$^2$ was about 900 Å since the
amorphous Si$_{1-x-y}$Ge$_x$C$_y$ layer about 900 Å thick started to
transform to an epitaxial layer at this fluence. No SiC and
Twin were observed from electron diffraction analysis. At
energy densities above 0.8 J/cm$^2$ the Ge concentration in the
upper surface of the Si$_{1-x-y}$Ge$_x$C$_y$ films was enriched with
the extent becoming more severe at higher energy densities
from EDS/cross-sectional TEM (XTEM) analysis. One example
is shown in Fig. 3, in which the strain contrast
associated with some defects is present in the upper surface
of the Si$_{1-x-y}$Ge$_x$C$_y$ film. It has been reported that surface
seggregation of Ge appears in the epitaxial growth of Si$_{1-x}$
Ge$_x$, presumably driven by the surface energy reduction
[23]. In the present study, laser annealing at higher energy
densities further enhanced this phenomenon. In addition, at
1.4 J/cm$^2$ Ge started to diffuse into the underlying Si sub-
strate, revealing that the melting depth at 1.4 J/cm$^2$ was
about 1500 Å, which was comparable to the thickness,
1500 Å, of the as-grown Si$_{0.76}$Ge$_{0.24}$ film. In contrast to
Ge the depth profile of C in the films annealed at an energy
density of 0.3–1.6 J/cm$^2$ remained nearly unchanged as in the
as-implanted film from SIMS analysis. One example is
shown in Fig. 4. The slight decrease of the ion yield for
the annealed Si$_{1-x-y}$Ge$_x$C$_y$ sample can be attributed to the
change of the chemical states of ions relatively to their
loosely bound states in the amorphous Si$_{1-x-y}$Ge$_x$C$_y$ film
after implantation [14].

At energy densities above 0.4 J/cm$^2$ significant amounts
of the implanted carbon were incorporated into substitu-
tional sites as evidenced by the peak of the substitutional C
(Cs) local vibration mode (LVM) at 607 cm$^{-1}$ shown in
Fig. 5. The concentration of substitutional C initially
increased with the energy density in the range of 0.4–
1.0 J/cm$^2$ and then saturated approximately at an energy
density of 1.0–1.6 J/cm$^2$. No SiC was formed. It has been
reported that the maximum concentration of C which can be
incorporated into substitutional site of Si or Si$_{1-x}$Ge$_x$ upon

![Fig. 2. XTEM image of an epitaxial Si$_{1-x-y}$Ge$_x$C$_y$ film grown at 0.4 J/
$^2$.](image2)
pulsed laser annealing is about 1.5% from XRD measurement, over which SiC is formed [14–17,19]. In the present study, the peak concentration of implanted C is about 2.0% calculated from the equation, $n = N_d / R_p$, where $n$ is the average dopant concentration in the region around $R_p$, $R_p$ is the projected range, and $N_d$ is the number of implanted C atoms per unit area [20]. Upon annealing the maximum concentration of C incorporated into the substitutional site may be lower than its peak concentration [11].

Upon annealing at 1.0 J/cm$^2$ for multiple pulses the concentration of substitutional C in the Si$_{1-x-y}$Ge$_x$C$_y$ films decreased with the pulse number, and the SiC peak at around 800 cm$^{-1}$ apparently appeared after irradiation of 20 pulses as shown in Fig. 6. This result is consistent with the plan-view TEM observation. The SIMS depth profiles in Fig. 7 for the sample annealed at 1.0 J/cm$^2$ for 20 pulses show that carbon segregated to the original amorphous/crystal interface and the surface of the film, where the C concentration could be high enough to form SiC. The presence of EOR defects in the original amorphous/crystal interface after laser annealing was confirmed by XTEM observation. This result implies that upon multiple pulse annealing the BOR defects play an important role in the gathering of C. Similar results have been reported in the formation of Si$_{1-x-y}$Ge$_x$C$_y$ by C$^+$ implantation and subsequent 700°C annealing [12]. The presence of EOR defects in conjunction with Ge segregation to the film surface could induce severe strain in the films. The driving force for reduction of the strain energy may be responsible for the enrichment of C in the film surface and the original amorphous/crystal interface upon pulsed laser annealing at 1.0 J/cm$^2$ for larger pulse numbers.

Kantor et al. [14] have reported that for the Si samples implanted with a carbon dose of $1 \times 10^{16}$/cm$^2$ and subse-
quent annealed at 1.0 J/cm² for one pulse no SiC was observed. This result is consistent with ours. However, in the case of 5 \times 10^{16}/\text{cm}² SiC appeared in the samples annealed at 1.0 J/cm² for 1–50 pulses. With increasing the pulse number the amount of SiC reduced, while that of the substitutional C in Si increased. Correspondingly, their SIMS data revealed that upon annealing for 3 pulses C started to diffuse deep into Si and the extent became more severe for higher pulse numbers. Comparing with the present study, it is evident that in addition to the annealing parameters the C concentration also plays an important role in the formation of SiC, Si₁₋ₓ₋ₓ GeₓCₓ, and Si₁₋ₓ₋ₓ GeₓCₓ by pulsed laser annealing.

From XRD analysis the implanted Si₁₋ₓ₋ₓ GeₓCₓ films were well crystallized after annealing at energy densities above 0.6 J/cm² as shown in Fig. 8. The satellite (004) peaks from the Si₁₋ₓ₋ₓ GeₓCₓ films grown at various energy densities are closer to the Si (004) peak than that from the as-grown Si₀.7₆Ge₀.2₄ film, indicating that the tensile stress in the Si₁₋ₓ₋ₓ GeₓCₓ films after laser annealing was smaller than that of the as-grown Si₀.7₆Ge₀.2₄ film. The reduction of the tensile stress in the Si₁₋ₓ₋ₓ GeₓCₓ films may result from combining the effects of substitutional C incorporation and Ge redistribution induced by pulsed laser annealing. In order to explore what extent Ge redistribution exerts on the reduction of the tensile stress in the Si₁₋ₓ₋ₓ GeₓCₓ films after laser annealing some as-grown Si₀.7₆Ge₀.2₄ films were annealed at energy densities ranging from 0.4 to 1.6 J/cm² and then followed by XRD analysis.

The XRD patterns in Fig. 9 show that after annealing at 1.0 J/cm² the position of (004) peak remains nearly unchanged except that it becomes slightly broadening as compared with that of the as-grown Si₀.7₆Ge₀.2₄ film. However, at energy densities above 1.4 J/cm² it shifts to higher angles because of Ge diffusion to the underlying Si substrate. Therefore, it can be concluded that for the Si₁₋ₓ₋ₓ GeₓCₓ films grown at energy densities below
1.0 J/cm² the reduction of tensile stress mainly results from the effect of substitutional carbon incorporation.

4. Summary and conclusions

For the Si₀.₇₆Ge₀.₂₄ films after C⁺ implantation at a dose of 1 × 10¹⁶/cm² epitaxial Si₁₋ₓ₋ₓₙₓGeₓCₓ films could be grown by subsequent pulsed KrF laser annealing at energy densities above 0.3 J/cm². At 0.8 J/cm² Ge segregation to the film surface was enhanced and Ge started to diffuse into the underlying Si at an energy density of 1.4–1.6 J/cm², while the depth profiles of C remained nearly unchanged as in the as-implanted Si₁₋ₓ₋ₓₙₓGeₓCₓ film. No SiC and twin defects were observed. Below 1.0 J/cm² the amount of substitutional carbon increased with the energy density, while above 1.0 J/cm² it nearly saturated. For the Si₁₋ₓ₋ₓₙₓGeₓCₓ films grown at 1.0 J/cm² for 5 and 20 pulses, respectively, SiC appeared and its amount increased with the pulse number because of C segregation to the film surface and the original amorphous/crystal interface where the EOR defects were present. For the Si₁₋ₓ₋ₓₙₓGeₓCₓ films grown at energy densities below 1.0 J/cm² the reduction of tensile stress mainly resulted from the effect of substitutional carbon incorporation.

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