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Characterization of $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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.

Keywords: $Si_{1-x-y}Ge_x C_y$ films; C^+ implantation; Pulsed laser annealing

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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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

*Corresponding author. E-mail: wtlin@mail.ncku.edu.tw

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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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ films was analyzed by X-ray diffraction (XRD) with Cu Kα radiation. The depth profile of C in the $Si_{1-x-y}Ge_xC_y$ films was examined by secondary ion mass spectrometry (SIMS). Absorption measurements were performed on a Fourier transform infrared spectrometer (FTIR). Samples with larger 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 $Si_{1-x-y}Ge_xC_y$ films were formed at 0.2 J/cm^2, while epitaxial $Si_{1-x-y}Ge_xC_y$ 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

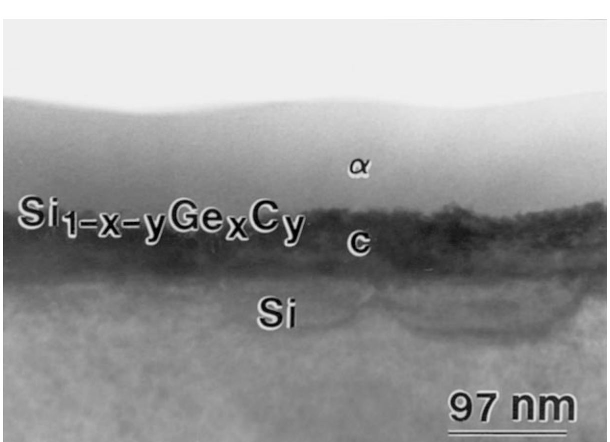

Fig. 1. XTEM image of the as-implanted $Si_{1-x}Ge_x$ film showing the formation of an amorphous $Si_{1-x-y}Ge_xC_y$ layer.

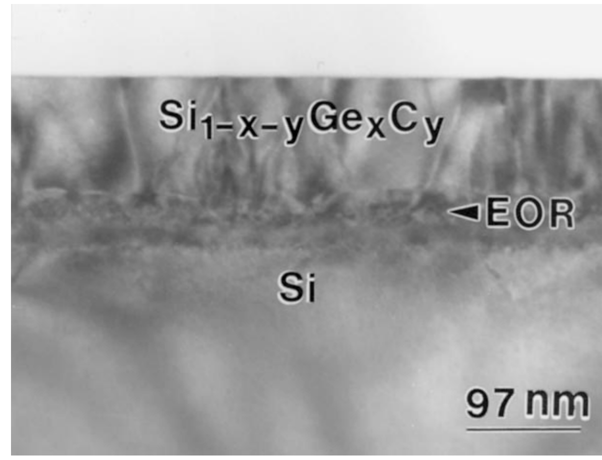

Fig. 2. XTEM image of an epitaxial $Si_{1-x-y}Ge_xC_y$ film grown at 0.4 J/cm^2.

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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ film. It has been reported that surface segregation 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 substrate, 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 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 $Si_{1-x-y}Ge_xC_y$ sample can be attributed to the change of the chemical states of ions relatively to their loosely bound states in the amorphous $Si_{1-x-y}Ge_xC_y$ film after implantation [14].

At energy densities above 0.4 J/cm^2 significant amounts of the implanted carbon were incorporated into substitutional 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

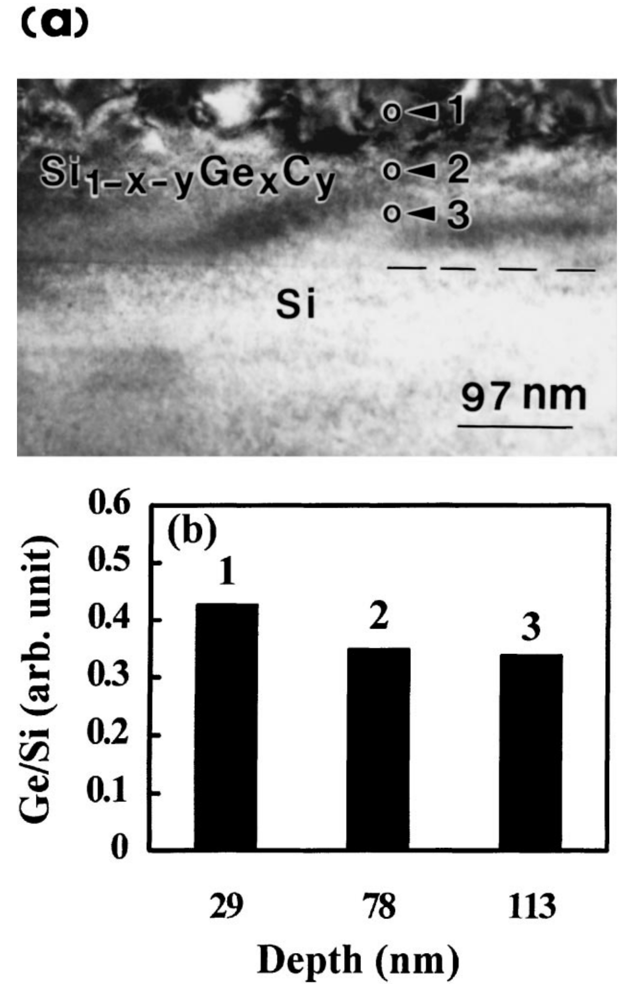

Fig. 3. (a) XTEM image and (b) Ge depth profile of a $Si_{1-x-y}Ge_xC_y$ film grown at 1.0 J/cm^2 showing the strong strain contrast and Ge segregation to the film surface. Ge/Si is the atomic concentration ratio, $x/(1-x)$, of $Si_{1-x}Ge_x$. The areas probed by the electron beam for EDS analysis are denoted as '0' and assigned as 1, 2, and 3, respectively.

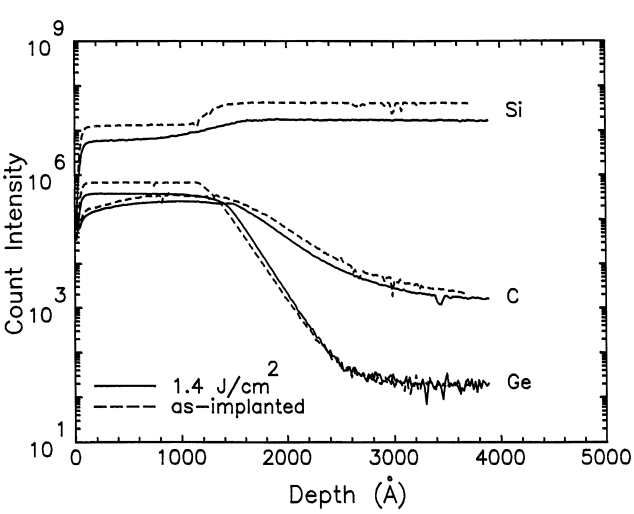

Fig. 4. SIMS depth profiles of Si, Ge, and C for the $Si_{1-x-y}Ge_xC_y$ film grown at 1.4 J/cm^2 and the as-implanted $Si_{1-x-y}Ge_xC_y$ film, respectively.

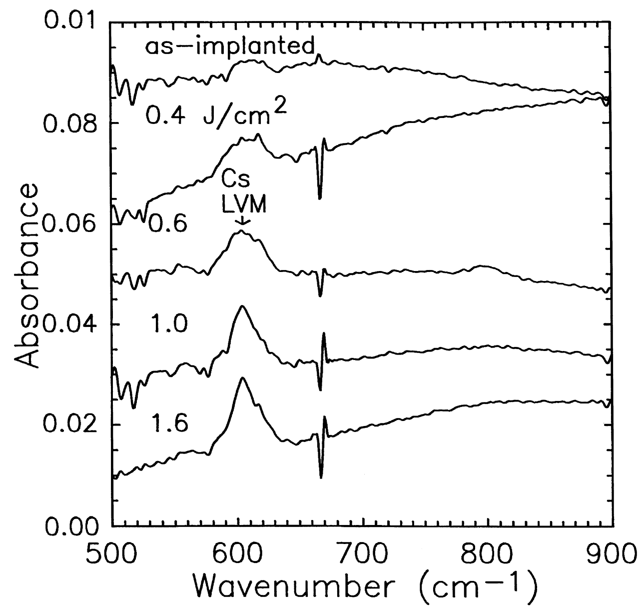

Fig. 5. FTIR absorbance spectra of the as-implanted $Si_{1-x-y}Ge_xC_y$ film and the epitaxial $Si_{1-x-y}Ge_xC_y$ films grown at various energy densities.

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 $_{1-x-y}Ge_xC_y$ 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 implys 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 $Si_{1-x}C_x$ 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 1×10^{16} /cm^2 and subse-

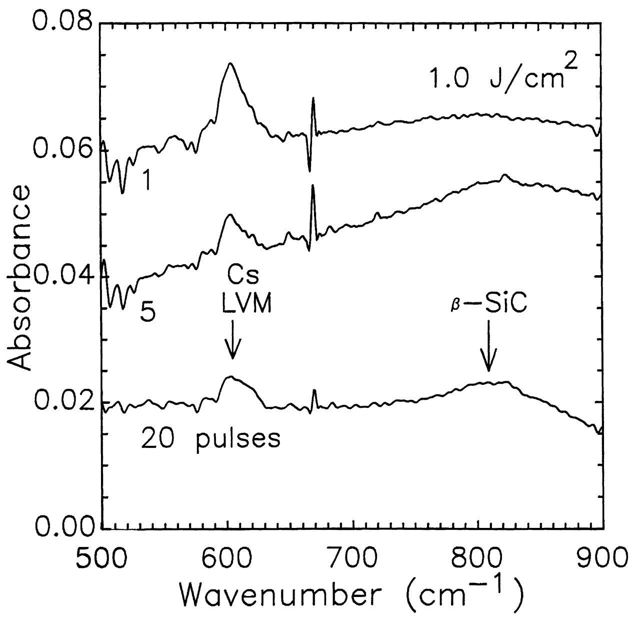

Fig. 6. FTIR absorbance spectra of the epitaxial $Si_{1-x-y}Ge_xC_y$ films grown at 1.0 J/cm^2 for various pulse number.

quently annealed at 1.0 J/cm^2 for one pulse no SiC was observed. This result is consistent with ours. However, in the case of 5×10^{16}/cm^2 SiC appeared in the samples annealed at 1.0 J/cm^2 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

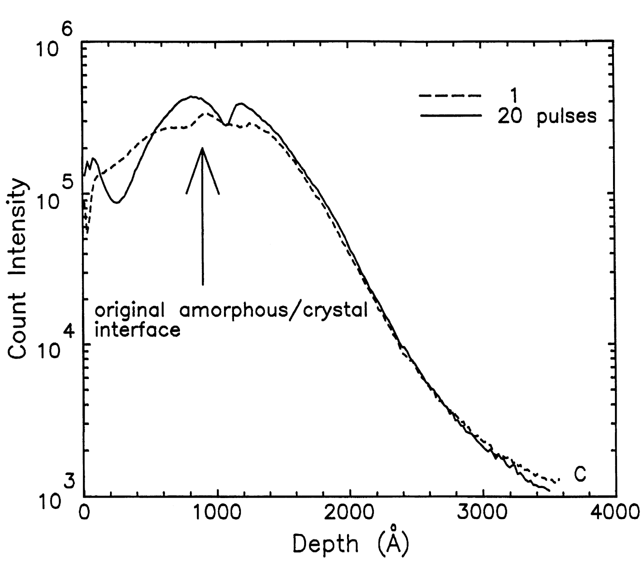

Fig. 7. SIMS depth profiles of C for the $Si_{1-x-y}Ge_xC_y$ films grown at 1.0 J/cm^2 for 1 and 20 pulses, respectively.

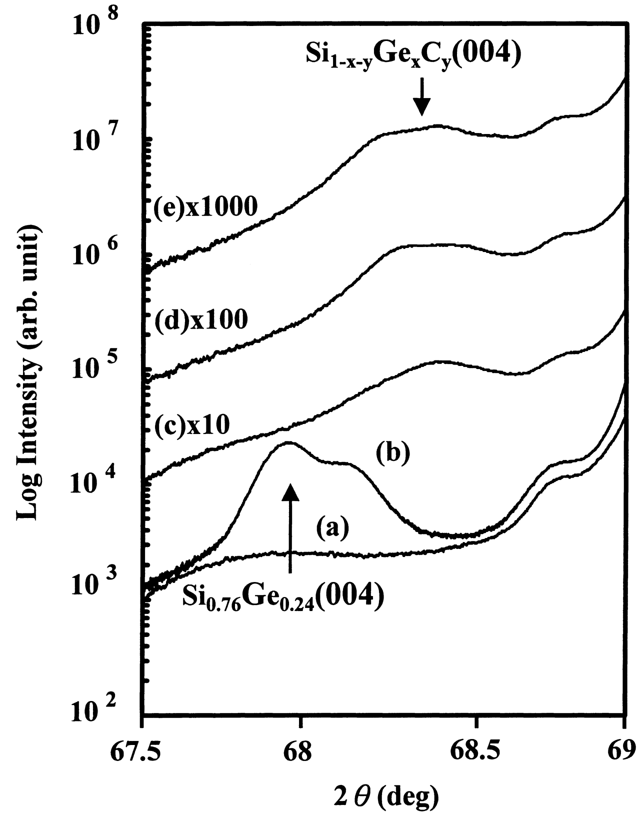

Fig. 8. XRD patterns of (a) the as-implanted $Si_{1-x-y}Ge_xC_y$ film, (b) the as-grown $Si_{0.76}Ge_{0.24}$ film, and the $Si_{1-x-y}Ge_xC_y$ films grown at (c) 0.6, (d) 1.0, and (e) 1.6 J/cm^2, respectively.

in the formation of SiC, $Si_{1-x}C_x$, and $Si_{1-x-y}Ge_xC_y$ by pulsed laser annealing.

From XRD analysis the implanted $Si_{1-x-y}Ge_xC_y$ films were well crystallized after annealing at energy densities above 0.6 J/cm^2 as shown in Fig. 8. The satellite (004) peaks from the $Si_{1-x-y}Ge_xC_y$ films grown at various energy densities are closer to the Si (004) peak than that from the as-grown $Si_{0.76}Ge_{0.24}$ film, indicating that the tensile stress in the $Si_{1-x-y}Ge_xC_y$ films after laser annealing was smaller than that of the as-grown $Si_{0.76}Ge_{0.24}$ film. The reduction of the tensile stress in the $Si_{1-x-y}Ge_xC_y$ 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 $Si_{1-x-y}Ge_xC_y$ films after laser annealing some as-grown $Si_{0.76}Ge_{0.24}$ films were annealed at energy densities ranging from 0.4 to 1.6 J/cm^2 and then followed by XRD analysis. The XRD patterns in Fig. 9 show that after annealing at 1.0 J/cm^2 the position of (004) peak remains nearly unchanged except that it becomes slightly broadening as compared with that of the as-grown $Si_{0.76}Ge_{0.24}$ film. However, at energy densities above 1.4 J/cm^2 it shifts to higher angles because of Ge diffusion to the underlying Si substrate. Therefore, it can be concluded that for the $Si_{1-x-y}Ge_xC_y$ films grown at energy densities below

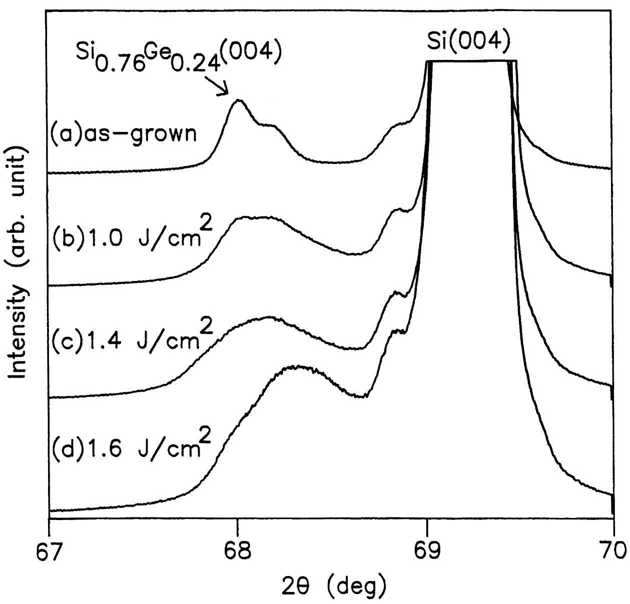

Fig. 9. XRD patterns of (a) the as-grown $Si_{0.76}Ge_{0.24}$ film, and the $Si_{0.76}Ge_{0.24}$ films annealed at (b) 1.0, (c) 1.4, and (d) 1.6 J/cm^2, respectively.

1.0 J/cm^2 the reduction of tensile stress mainly results from the effect of substitutional carbon incorporation.

4. Summary and conclusions

For the $Si_{0.76}Ge_{0.24}$ films after C^+ implantation at a dose of 1×10^{16}/cm^2 epitaxial $Si_{1-x-y}Ge_xC_y$ films could be grown by subsequent pulsed KrF laser annealing at energy densities above 0.3 J/cm^2. At 0.8 J/cm^2 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/cm^2, while the depth profiles of C remained nearly unchanged as in the as-implanted $Si_{1-x-y}Ge_xC_y$ film. No SiC and twin defects were observed. Below 1.0 J/cm^2 the amount of substitutional carbon increased with the energy density, while above 1.0 J/cm^2 it nearly saturated. For the $Si_{1-x-y}Ge_xC_y$ films grown at 1.0 J/cm^2 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 $Si_{1-x-y}Ge_xC_y$ 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.

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References

[1] J.C. Bean, Proc. IEEE 80 (1992) 571.
[2] H. Presting, H. Kibbel, M. Jaros, R.M. Turton, U. Menczigar, G. Abstreiter, H.G. Grimmeiss, Semicond. Sci. Technol. 1 (1992) 1127.
[3] R.A. Soref, J. Appl. Phys. 70 (1991) 2470.
[4] A.A. Demkov, O.F. Sankey, Phys. Rev. B 48 (1993) 2207.
[5] J.L. Regolini, S. Bodnar, J.C. Oberlin, F. Ferrieu, M. Gauneau, B. Lambert, P. Bucaud, J. Vac. Sci. Technol. A 12 (1994) 1015.
[6] K. Eberl, S.S. Iyer, S. Zoller, J.C. Tsang, F.K. LeGoucs, Appl. Phys. Lett. 60 (1991) 3033.
[7] H.J. Osten, E. Bugiel, P. Zaumseil, Appl. Phys. Lett. 64 (1994) 3440.
[8] R. Boucaud, C. Francis, F.H. Julien, J.M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert, J.L. regolini, Appl. Phys. Lett. 64 (1994) 875.
[9] Z. Atzmon, A.E. Bair, E.J. Jacquez, J.W. Mayer, D. Chandrasekhar, D.J. Smith, R.L. Hervig, McD. Robinson, Appl. Phys. Lett. 65 (1994) 2559.
[10] J.W. Strane, H.J. Stein, S.R. Lee, B.L. Doyle, S.T. Picraux, J.W. Mayer, Appl. Phys. Lett. 63 (1994) 2786.
[11] X. Lu, N.W. Cheung, Appl. Phys. Lett. 699 (1996) 1915.
[12] J.W. Strane, S.R. Lee, H.J. Stein, S.T. Picraux, J.K. Watanabe, J.W. Mayer, J. Appl. Phys. 79 (1996) 637.
[13] S.C. Jain, H.J. Osten, B. Dietrich, H. Rucker, Semicond. Sci. Technol. 10 (1995) 1289.
[14] Z. Kantor, E. Fogarassy, A. Grob, J.J. Grob, D. Muller, B. Prevot, R. Stuck, Appl. Phys. Lett. 69 (1996) 969.
[15] K.M. Kramer, M.O. Thompson, J. Appl. Phys. 79 (1996) 4118.
[16] E. Fogarassy, A. Grob, J.J. Grob, D. Muller, B. Prevot, R. Stuck, S. deUnamuno, P. Boher, M. Stehle, SPIE 2991 (1997) 202.
[17] A. Grob, J.J. Grob, D. Muller, B. Prevot, R. Stuck, F. Fogarassy, Thin Solid Films 294 (1997) 145.
[18] J. Boulmer, P. Boucaud, C. Guedj, D. Debarre, D. Bouchier, E. Finkman, S. Prawer, K. Nugent, A. Desmur-Larre, C. Godet, P. Rocai Cabarrocas, J. Cryst. Growth 157 (1995) 436.
[19] E. Fogarassy, A. Grob, J.J. Grob, D. Muller, B. Prevot, S. de Unamuno, P. Boher, M. Stehle, Mater. Chem. Phys. 54 (1998) 153.
[20] J.P. Biersack, L.G. Haggmark, Nucl. Instrum. Methods 174 (1980) 257.
[21] S. De Unamuno, E. Fogarassy, Appl. Surf. Sci. 36 (1989) 1.
[22] P. Baeri, E. Rimini, Mater. Chem. Phys. 46 (1996) 169.
[23] D.E. Jesson, S.J. Pennycook, J.-M. Baribeau, Phys. Rev. Lett. 66 (1991) 750.