Effects of high temperature rapid thermal annealing on Ge films grown on Si(001) substrate*

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Tensile strain, crystal quality, and surface morphology of 500 nm thick Ge films were improved after rapid thermal annealing at 900 °C for a short period (< 20 s). The films were grown on Si(001) substrates by ultra-high vacuum chemical vapor deposition. These improvements are attributed to relaxation and defect annihilation in the Ge films. However, after prolonged (> 20 s) rapid thermal annealing, tensile strain and crystal quality degenerated. This phenomenon results from intensive Si–Ge mixing at high temperature.

Keywords: Ge film, rapid thermal annealing, tensile strain, Si–Ge mixing

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1. Introduction

In recent years, Ge on Si substrate has been extensively studied for Si-based electronic and optoelectronic device applications[1–4] because of its compatibility with complementary metal oxide semiconductor (CMOS) processes, high carrier mobility, and pseudo direct bandgap structure. A tensile strain in high-quality Ge can enhance the carrier mobility and decrease the energy difference (140 meV) between its direct and indirect band gaps, which can be used in applications such as high-speed transistors,[5] infrared photodetectors,[6] and light emitters.[7] Considerable effort has been focused on increasing the tensile strain in Ge films. Despite the enhanced tensile strain (> 1%) achieved by techniques such as the use of larger-lattice substrates[8] and micromechanical strain engineering,[9] many disadvantages limit the application of these particular methods. These disadvantages include poor quality and process complexity. The most common approach to introducing a tensile strain into Ge films is using the thermal expansion difference between Ge and Si. The growth temperature must be increased to enhance the tensile strain. However, growing Ge films at high temperatures (> 800 °C) increases the Si–Ge mixing and surface roughening. Cyclic annealing at 900 °C, repeated several times, can reduce threading dislocations in Ge film on Si.[10] However, this complex process is time consuming. In addition, this method can also enhance the Si–Ge mixing as the interdiffusion is a time-dependent behavior.

In the present work, Ge films on Si were annealed at 900 °C with varying time intervals by rapid thermal annealing (RTA). The tensile strain, crystal quality, and surface morphology of the Ge films were investigated. The improvement and subsequent degeneration of the tensile strain and the crystal quality of the samples were observed after the RTA, and the possible reason for this phenomenon is discussed.

2. Experimental details

The samples were grown by cold-wall ultrahigh vacuum chemical vapor deposition on Si(001) substrates, using pure disilane (Si_2H_6) and germane (GeH_4). The Si substrates (resistivity of 1000 Ω·cm) were first cleaned using an *ex situ* improved Radio Corporation of America (RCA) wet-chemical cleaning recipe, and then loaded into the pre-treatment chamber. Before growth, the substrate was degassed at 300 °C in the pre-treatment chamber, and then heated up to 920 °C for 5 min in the growth chamber with a background pressure lower than 1×10^{-7} Pa for deoxidization. A 50 nm low temperature Ge buffer layer was deposited at 290 °C. Next, a 450 nm high temperature Ge layer was grown at 600 °C on the 50 nm Ge buffer layer. *Ex situ* RTA was used to heat the samples up to 900 °C with a ramp up rate of 50 °C/s for varying time (5 s, 10 s, 20 s, 30 s, 45 s, 60 s) in N_2 atmosphere. X-ray diffraction (XRD) measurements in the (004) and (224) directions using the Cu-$K_{\alpha1}$ ($\lambda = 0.15406$ nm) X-ray source and Raman measurements were performed to estimate the strain status and the crystal quality of the Ge films. Raman measurements were performed using a LabRam HR 800 Raman instrument at room temperature with a 633 nm He–Ne laser and a liquid N_2 cooled InGaAs photodetector. The diffusion depths of Si atoms into the Ge films were obtained by secondary ion mass spectrometry (SIMS). The surface morphology of the samples was examined by atomic force microscopy (AFM) performed in contact mode. Details of material growth

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can be found in our previous work.[11]

3. Results and discussion

XRD measurements in the (004) direction of the samples annealed at 900 °C with varying time intervals are depicted in Fig. 1(a). The XRD peaks of the Ge films after RTA show an appreciable shift to higher 2θ angles with respect to those of the as-grown Ge sample, which indicates the increased tensile strain in the Ge films. To characterize the tensile strain in the Ge films accurately, XRD measurements in the (224) direction of the samples were performed. For the Ge epitaxial films on Si(001), the in-plane strain $\varepsilon_{||}$ and the strain perpendicular to the film $\varepsilon_{\perp}$ can be determined from the XRD data by

$$\varepsilon_{\perp} = \varepsilon_{004}; \quad \varepsilon_{||} = 3\varepsilon_{224} - 2\varepsilon_{004}, \tag{1}$$

where ε_{004} and ε_{224} are the strains in the (004) and (224) directions of the Ge film, respectively. Table 1 summarizes the strain statistical analysis of the samples. Results show that compared with the as-grown sample, the tensile strain after RTA treatment increases by at least 40%. The highest tensile strain of 0.208% is obtained after 10 s RTA at 900 °C, which shows a 60% increase compared with the as-grown sample. The relaxation of the Ge films at high temperature and the thermal expansion difference between Ge and Si are responsible for this tensile strain enhancement.[12] The tensile strain in the Ge films increases after RTA but decreases with annealing time longer than 20 s. This phenomenon has not previously been reported. In principle, with increased annealing time, the tensile strain should remain close to the maximum strain. The maximum strain is determined by three factors: temperature, thermal expansion difference, and residual compressive strain.[13] However, the strain change induced by the Si–Ge mixing under RTA should not be disregarded. Intermixing is a time-dependent behavior. At high temperatures (900 °C), the Si–Ge mixing at the Si–Ge interface becomes very intensive.[14] The diffusion of Si atoms into the Ge films can offset and release the tensile strain. Besides, the tensile strain of the Ge films on Si originates from stretching between the Si substrate and the Ge film at the Ge/Si interface. A Ge/Si interface blur induced by intense Si–Ge mixing is another possible reason for the decrease of the tensile strain. In Fig. 1(a), the trend of the Si–Ge mixing after RTA treatment can be observed clearly. The various shoulders next to the Ge peaks at high 2θ angles correspond to the varying intensities of Si–Ge mixing. The atom's vertical distributions in the as-grown sample and the sample after 60 s RTA at 900 °C by SIMS are shown in Fig. 2, revealing that the Ge/Si interface of the as-grown sample is abrupt. An intense Si–Ge mixing of the sample after 60 s RTA at 900 °C also can be observed. The diffusion depth of Si atoms into the Ge film is about 100 nm. This Si–Ge mixing trend explains the reduction in the tensile strain. The $\varepsilon_{||}/\varepsilon_{\perp}$ obtained from our measurements is about -1.36 ± 0.07, which agrees with a previous report.[12] This result indicates the accuracy of the XRD strain measurements.

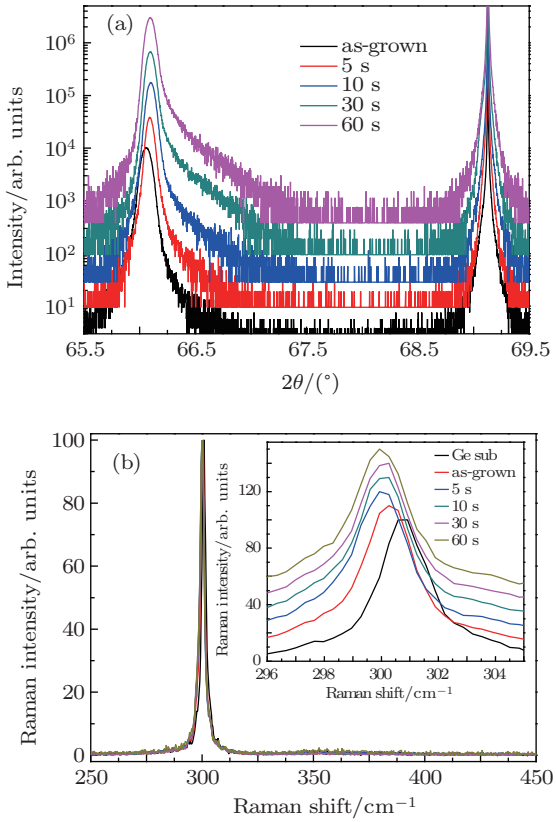


Fig. 1. (color online) (a) XRD curves of the samples in the (004) direction. (b) Normalized Raman spectra of the Ge substrate, the as-grown sample, and the annealed samples.

Table 1. Summary of the strain statistics analysis of samples.

Annealing condition	XRD				Raman
	ε_{004}, $\varepsilon_{\perp}$/%	ε_{224}/%	$\varepsilon_{||}$/%	$\varepsilon_{||}/\varepsilon_{\perp}$	$\varepsilon_{||}$/%
As-grown	–0.0932±0.0015	–0.0192±0.0020	0.129±0.006	–1.38±0.05	0.135±0.008
900 °C 5 s	–0.1366±0.0015	–0.0266±0.0025	0.194±0.008	–1.41±0.07	0.209±0.008
900 °C 10 s	–0.1502±0.0015	–0.0308±0.0025	0.208±0.008	–1.38±0.07	0.197±0.008
900 °C 20 s	–0.1529±0.0015	–0.0327±0.0025	0.208±0.008	–1.36±0.07	0.195±0.008
900 °C 30 s	–0.1452±0.0015	–0.032±0.003	0.195±0.009	–1.34±0.08	0.198±0.008
900 °C 45 s	–0.1456±0.0015	–0.034±0.003	0.190±0.009	–1.30±0.08	0.197±0.008
900 °C 60 s	–0.1407±0.0015	–0.032±0.003	0.185±0.009	–1.31±0.08	0.199±0.008

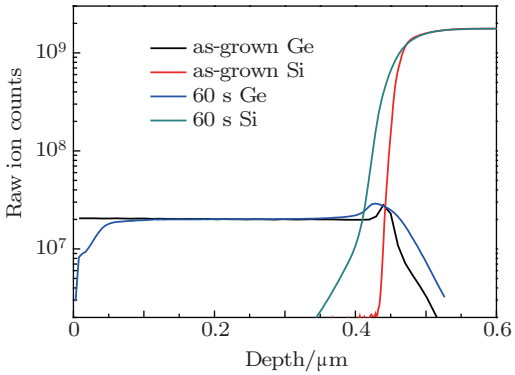


Fig. 2. (color online) The atom's vertical distributions of the as-grown sample and the sample after 60 s RTA at 900 °C.

Te Raman measurements of the Ge films were examined to confirm the accuracy of the XRD results. The normalized Raman spectra of the Ge substrate and the samples are shown in Fig. 1(b). Compared with the as-grown Ge sample or Ge substrate, a significant low shift in the RTA samples is observed, which shows the tensile strain in the Ge films. The in-plane strain $\varepsilon_{||}$ can be determined from the Raman data by[15]

$$\varepsilon_{||} = \frac{\omega_{\text{bulk Ge}} - \omega_{\text{Ge-Ge}} - 16(1-x)}{385}, \qquad (2)$$

where $\omega_{\text{bulk Ge}}$ and $\omega_{\text{Ge-Ge}}$ are the Raman peaks of the Ge–Ge vibration mode of bulk Ge and GeSi films, respectively, and x is the Ge content in the GeSi alloy. Within the 633 nm light penetration depth (< 100 nm), no obvious Si–Ge vibration mode can be observed in Fig. 1(b). Therefore, x is approximately equal to 1, and the sample strain is calculated from the Raman shift of the Ge–Ge vibration mode. Lorentz fitting of the Raman peaks is necessary to enhance the accuracy of the estimates. The strain results are shown in Table 1. The strain results determined from the Raman spectra are slightly larger than the XRD results. This difference is due to the limited penetration depth of the 633 nm laser used in the Raman measurements. However, the Raman results are in good agreement with the XRD results, indicating the accuracy of the XRD measurements.

The full widths at half maximum (FWHM) of XRD and Raman peaks are used to estimate the crystal quality of the Ge films. After RTA, a remarkable decrease in peak FWHM is observed both in the XRD and the Raman measurements, indicating an improvement in Ge quality (Fig. 3). Within 20 s RTA, the XRD FWHM of the samples is reduced by at least 35%. The FWHM of the Raman peak of the Ge film after 10 s RTA is about 2.27 cm^{-1}, which is closer to that of the Ge substrate (2.15 cm^{-1}). This result indicates the high quality of the Ge films. This improvement in quality is attributed to the annihilation of dislocations and defects induced by the high-temperature technique.[10] Despite the enhancement of the Ge films after RTA, an increasing trend in FWHM is observed. This phenomenon can likewise be explained as the result of the varying intensities of Si–Ge mixing. The diffusion of Si atoms into the Ge films can change the lattice and broaden the FWHM of peaks. The difference in trends between the XRD results and the Raman results (Fig. 3) is also due to the limited penetration depth of the 633 nm laser used in the Raman measurements.

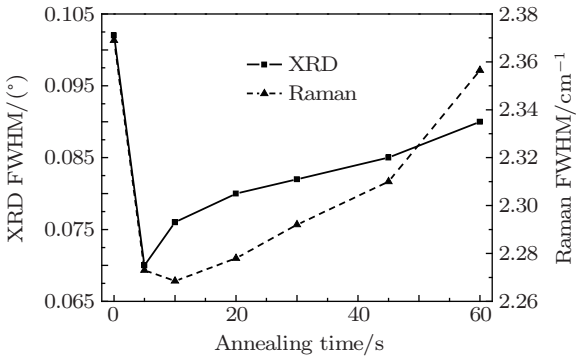


Fig. 3. XRD and Raman FWHM of the samples annealed at 900 °C with varying time intervals.

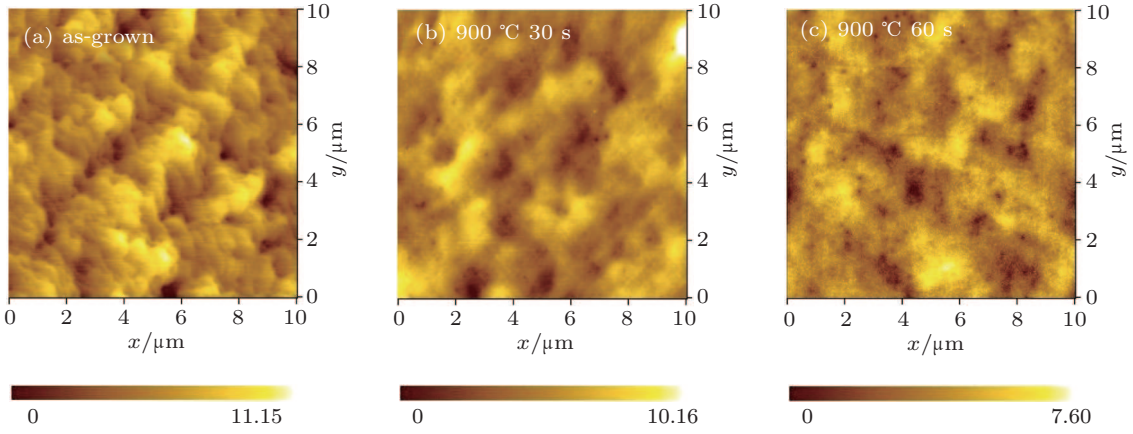


Fig. 4. (color online) AFM images (10 μm × 10 μm) of (a) as-grown samples and the samples annealed at 900 °C for (b) 30 s and (c) 60 s.

Surface morphology of the samples after RTA was also studied. The 10 μm×10 μm AFM images of the samples are shown in Fig. 4. After RTA, the surfaces of the samples become smoother, and the root mean square (RMS) surface roughness decreases from 1.6 nm to 1.1 nm. A similar morphology was described previously.[13,16] At high temperatures, the escape, migration, and reconstruction of surface atoms explain this behavior. Although the RTA can smooth the sample surface, dislocation grids and pits are observed after prolonged annealing time (> 30 s), which is another reason for the increase of FWHM and the reduction of strain in longer RTA treatments.

4. Conclusion

In summary, high-temperature RTA can effectively and easily improve the tensile strain and crystal quality of Ge on Si. This improvement is attributed to relaxation and defect annihilation in Ge films. The optimum annealing time is within 20 s, which prevents the degeneration of both crystal quality and tensile strain that is induced by the Si–Ge mixing. This study is significant for Ge/Si heterostructures and Ge/Si device fabrication.

References

[1] Chui C O, Ramanathan S, Triplett B B, McIntyre P C and Saraswat K C 2002 *IEEE Electron Device Lett.* **23** 473

[2] Miyao M, Murakami E, Etoh H, Nakagawa K and Nishida A 1991 *J. Cryst. Growth* **111** 912

[3] Hu W X, Cheng B W, Xue C L, Zhang G Z, Su S J, Zuo Y H and Wang Q M 2012 *Chin. Phys. B* **21** 017805

[4] Li Y M, Hu W X, Cheng B W, Liu Z and Wang Q M 2012 *Chin. Phys. Lett.* **29** 034205

[5] Moriyama Y, Kamimuta Y, Ikeda K and Tezuka T 2012 *Thin Solid Films* **520** 3236

[6] Liu J F, Cannon D D, Wada K, Ishikawa Y, Jongthammanurak S, Danielson D T, Michel J and Kimerling L C 2005 *Appl. Phys. Lett.* **87** 011110

[7] Chen Y H, Li C, Zhou Z W, Lai H K, Chen S Y, Ding W C, Cheng B W and Yu Y D 2009 *Appl. Phys. Lett.* **94** 141902

[8] Huo Y, Lin H, Chen R, Makarova M, Rong Y, Li M, Kamins T I, Vuckovic J and Harris J S 2011 *Appl. Phys. Lett.* **98** 011111

[9] Lim P H, Park S, Ishikawa Y and Wada K 2009 *Opt. Express* **17** 16358

[10] Luan H C, Lim D R, Lee K K, Chen K M, Sandland J G, Wada K and Kimerling L C 1999 *Appl. Phys. Lett.* **75** 2909

[11] Hu W X, Cheng B W, Xue C L, Xue H Y, Su S J, Bai A Q, Luo L P, Yu Y D and Wang Q M 2009 *Appl. Phys. Lett.* **95** 092102

[12] Liu J, Cannon D D, Wada K, Ishikawa Y, Danielson D T, Jongthammanurak S, Michel J and Kimerling L C 2004 *Phys. Rev. B* **70** 155309

[13] Capellini G, De Seta M, Zaumseil P, Kozlowski G and Schroeder T 2012 *J. Appl. Phys.* **111** 073518

[14] Hasanuzzaman M, Haddara Y M and Knights A P 2009 *J. Appl. Phys.* **105** 043504

[15] Tsang J C, Mooney P M, Dacol F and Chu J O 1994 *J. Appl. Phys.* **75** 8098

[16] Nayfeh A, Chui C O, Saraswat K C and Yonehara T 2004 *Appl. Phys. Lett.* **85** 2815