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Abstract. Raman spectroscopy has been employed to investigate the microstructural features of strained Si–Ge layers deposited by the rapid-thermal-process very-low-pressure chemical vapour deposition method. Auger electron spectroscopy was used to determine the Ge concentrations in the Si–Ge layers. The Ge atoms in the high-Ge-concentration Si–Ge alloy are distributed more homogeneously and randomly than in the low-Ge-concentration alloy. The substrate temperature has a great influence on the microstructure of the strained Si–Ge alloy. A high Ge content needs a relatively low substrate temperature to deposit high-quality Si–Ge alloy, but a low Ge content requires a higher growth temperature during the deposition of the Si–Ge alloy.

1. Introduction

Great progress has been made in the use of strained Si–Ge alloys in Si–Ge-based heterojunction bipolar transistors and its optical properties have shown great potential. However, the optical and electronic characteristics and the potential for applying strained Si–Ge alloys depend on the microstructural properties. It has been found that the atoms and strain distribution in strained Si–Ge alloys have a great influence on the quality and characteristics.

Raman spectroscopy has proved to be a powerful technique for characterizing Si–Ge alloys. This is based on the model that Ge atoms are distributed homogeneously and randomly in the Si–Ge alloys [1–3]. However, the precise control of the uniformity and distribution of dopants in small dimensions during growth have been limited for several reasons [4, 5]. The microstructural properties of Si–Ge alloys have a great dependence on the very-low-pressure chemical vapour deposition (VLPCVD) reaction parameters such as substrate temperature and GeH$_4$-to-SiH$_4$ flow ratio. In this paper, we studied the effect of temperature and composition on the microstructure in Si–Ge alloys using Raman scattering.

2. Experiment and results

The samples were grown on Si(100) substrates by rapid-thermal-process (RTP) VLPCVD [6]. The thickness of the Si$_{1-x}$Ge$_x$ alloy was smaller than the critical thickness at the Ge concentration x, so the Si–Ge alloy was strained. The growth substrate temperature was changed from 620 to 750 °C. Changing the GeH$_4$-to-SiH$_4$ ratio of the reaction gases, we deposited Si–Ge alloys of different Ge concentrations. The growth pressure was about 10 mTorr. The Si–Ge alloys were analysed by auger electron spectroscopy (AES) (Phi 550,

instrument); Ar^+ sputtering at an energy of 1.5 keV and an angle of 50° was used to obtain the AES depth profiles. Standard $Si_{0.5}Ge_{0.5}$ alloy (fabricated by Si–MBE) has been employed to determine the Ge concentration in the Si–Ge alloy from Auger signals of Si (LVV, 92 eV) and Ge (LMM, 1147 eV). The O (KLL, 503 eV) and C (KLL, 272 eV) Auger signals were recorded to determine the contamination from oxygen and carbon atoms. It was found that the concentrations of oxygen and carbon atoms in the Si–Ge alloys were nearly 1.0×10^{18} cm^{-3} and 2.5×10^{18} cm^{-3}, respectively.

The Raman spectra of Si–Ge alloys were recorded at room temperature on a Spex Raman spectrometer in a quasi-back-scattering geometry using argon laser light at 300 mW and 488 nm for excitation. The wavenumber resolution was 0.5 cm^{-1}. A standard Si sample was used to calibrate the wavenumber of the monochromator.
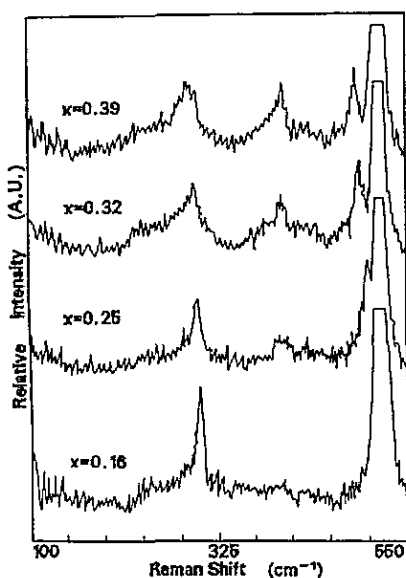

Figure 1. The Raman spectra of Si–Ge alloys of different Ge concentrations (the first group of samples) deposited at a constant SiH_4 flow rate of 1.5 sccm (A.U., arbitrary units). The GeH_4 flow rate was changed from 0.11 to 0.3 sccm. The substrate temperature was 620 °C.
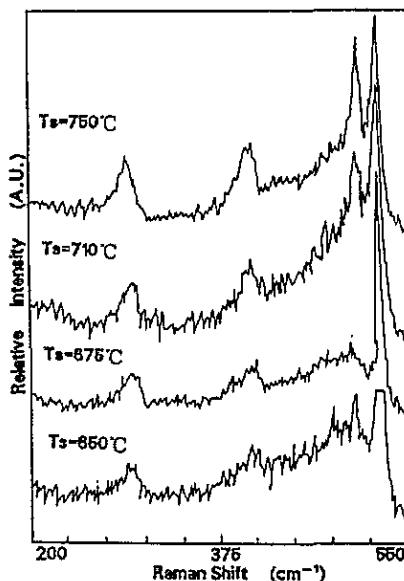
Figure 2. The Raman spectra of Si–Ge alloys (the second group of samples) deposited at the same SiH_4 and GeH_4 flow rates at different substrate temperatures (A.U., arbitrary units). The SiH_4 flow rate was 1.5 sccm, and the GeH_4 flow rate was 0.2 sccm. The substrate temperatures were 650, 675, 710 and 750 °C.

Figure 1 shows the Raman spectra of Si–Ge alloys of different Ge concentrations (the first group of samples) deposited at a constant SiH_4 flow rate of 1.5 sccm. The GeH_4 flow rate was changed from 0.11 to 0.3 sccm. The substrate temperature was 620 °C. As the Ge concentration in Si–Ge alloys changed from 0.16 to 0.39, the Ge–Ge Raman peak shifted from 304 to 292 cm^{-1}, the Si–Si Raman peak shifted from 508 to 494 cm^{-1}, and the full width at half-maximum (FWHM) of the Ge–Ge Raman peak changed from 7 to 25 cm^{-1}.

Figure 2 shows the Raman spectra of Si–Ge alloys (the second group of samples) deposited at the same SiH_4 and GeH_4 flow rates but at different substrate temperatures. The SiH_4 flow rate was 1.5 sccm; the GeH_4 flow rate 0.2 sccm. The substrate temperatures were 650, 675, 710 and 750 °C respectively. Figure 3 shows the Ge concentration in Si–Ge alloys of the second group plotted against substrate temperature for the same SiH_4 and GeH_4 flow
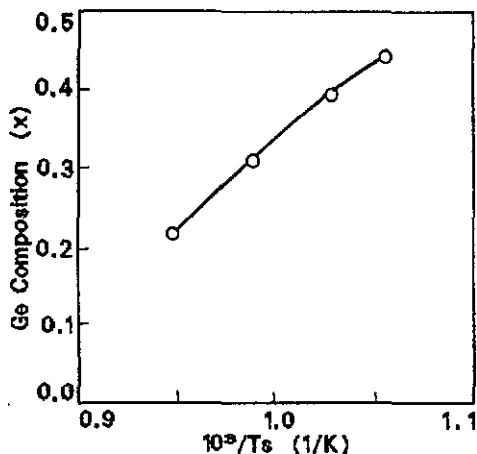
Figure 3. Ge concentration in Si–Ge alloys of the second group against substrate temperature deposited at the same SiH₄ and GeH₄ flow rates.

rates. As the substrate temperature changed from 650 to 750 °C, the Ge concentration in the Si–Ge alloys was changed from 0.23 to 0.46, the Ge–Ge Raman peak shifted from 287 to 298 cm^{-1}, the Si–Si Raman peak shifted from 508 to 496 cm^{-1}, and the FWHM of the Ge–Ge Raman peak changed from 14 to 21 cm^{-1}.
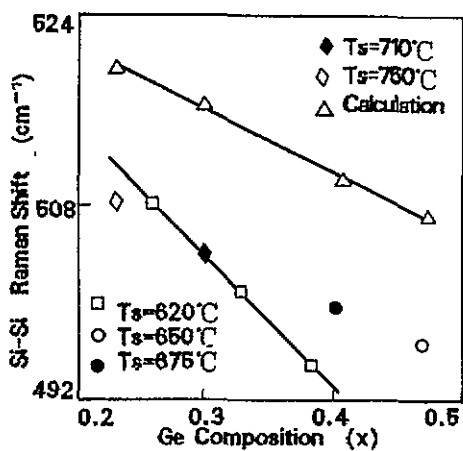

Figure 4. The Raman shift of the Si–Si Raman peak against Ge concentration in the Si–Ge layers (the first and second groups of samples). The calculation results for fully strained Si–Ge alloy are also shown.

Figure 5. The Raman shift of the Ge–Ge Raman peak against the Ge concentration in the Si–Ge layers (the first and second groups of samples). The calculation results for fully strained Si–Ge alloy are also shown.

Figures 4 and 5 show the Raman shifts of Si–Si and Ge–Ge Raman peaks, respectively, against Ge concentration in the Si–Ge layers (the first and second groups of samples). The calcu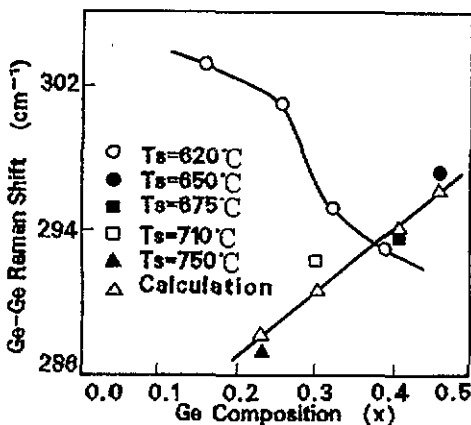lation results for fully strained Si–Ge alloy are also shown in figures 4 and 5, where we have assumed that the atoms are distributed randomly and homogeneously.

Figure 6 is the FWHM of the Ge–Ge Raman peak against the Ge concentration in the Si–Ge layers.
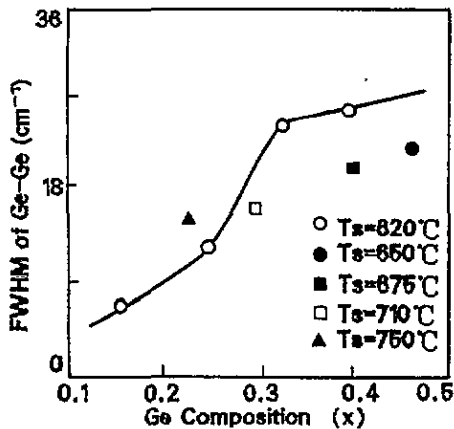
Figure 6. The FWHM of the Ge–Ge Raman peak against the Ge concentration in the Si–Ge layers (the first and second groups of samples).

3. Discussion

The VLPCVD reaction is a surface-controlled reaction including the adsorption of SiH_4 and GeH_4 and the desorption of hydrogen on the surface which limited reaction. A high temperature leads to a reduction in the SiH_4 and GeH_4 sticking coefficients, but the sticking coefficients of SiH_4 and GeH_4 do not change to the same degree. The activation energy of the SiH_4 sticking coefficient is higher than that of the GeH_4 sticking coefficient; this difference between the activation energies of the sticking coefficients of silane and germane leads to a small dependence of Ge concentration on temperature at constant flow rates.

Raman scattering has been used to characterize Si–Ge alloys by following the behaviours of three principal optical phonon modes: Ge–Ge vibration at around 300 cm^{-1}, Ge–Si vibration at around 400 cm^{-1}, and Si–Si vibration near 500 cm^{-1}. In a random alloy, the numbers of Si–Si, Ge–Si and Ge–Ge bonds are proportional to $(1-x)^2$, $2x(1-x)$ and x^2, respectively, where x is the Ge concentration of the $Si_{1-x}Ge_x$ alloy [1]. Increasing the Ge concentration will increase the strain in the Si–Ge alloy and so shift the Ge–Ge Raman peak to a high frequency and the Si–Si Raman peak to a low frequency. The FWHM of a Raman peak caused by different vibration frequencies of the atoms represents the structure of the alloy. The random homogeneous distribution of atoms in the alloy will cause the FWHM to increase.

In fact, the distribution of Ge atoms is not always homogeneous in Si–Ge alloys, especially in strained Si–Ge alloys. Generally, if the Ge atoms are distributed homogeneously, the Si–Ge alloy will have a low free energy but, if the Ge or Si atoms have sufficient energy (e.g. under the effect of strain) to migrate to the high-energy position during the Si–Ge alloy growth, it may be possible for the Ge atoms to be distributed inhomogeneously.

A high temperature or high Ge concentration leads to sticking coefficients to decrease and the desorption rate of hydrogen to increase; so the surface coverage will reduce. Then the atom mobility increases as the temperature and composition increase. However, different from the strain effect on atom migration, the temperature and alloy concentration increase the mobility isotopically and cause the atoms to migrate in all directions; so the atoms may be distributed more homogeneously in Si–Ge alloys. As the homogeneous distribution of atoms will cause the strain to be distributed homogeneously, there may be a smaller strain on Ge atoms in the high-Ge-concentration Si–Ge alloys where the Ge atoms are distributed homogeneously.
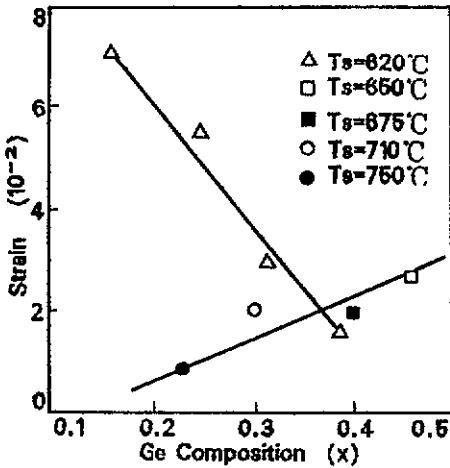
Figure 7. The strain on Ge atoms against Ge concentration in the Si–Ge layers (the first and second groups of samples).
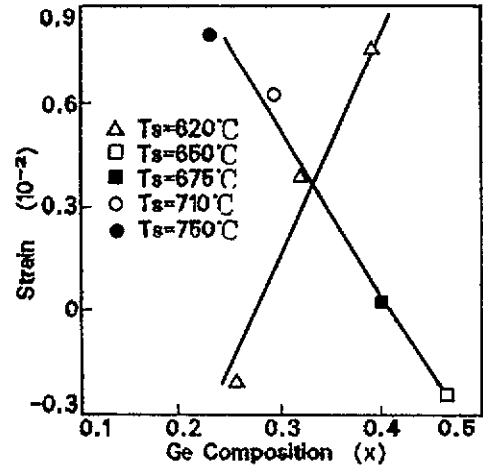
Figure 8. The strain on Si atoms against Ge concentration in the Si–Ge layers (the first and second groups of samples).

The stress in strained Si–Ge alloys is proportional to the strain or the ratio of the phonon shift over the Raman shift of the unstrained alloy [3]. Figures 7 and 8 show the strains in the Si–Ge alloys calculated from the Ge–Ge Raman shift and Si–Si Raman shift, respectively. We can see that, in the first group, the strain on Ge atoms decreases but the strain on Si atoms increases as the Ge concentration increases. This shows that the distribution of the strain and the Ge atoms has changed from inhomogeneous to relatively homogeneous when the Ge concentration increases in the Si–Ge alloys. The homogeneous distribution of Ge atoms will cause the FWHM of the Ge–Ge peak to increase as the Ge concentration increases, as shown in figure 6.

The decreasing Ge concentration in Si–Ge alloys will inhibit Ge atom migration. So, in low-Ge-concentration alloys, it may become difficult for Ge atoms to migrate from the sites of deposition to lower-free-energy positions and so they are distributed inhomogeneously. However, a high temperature will cause the atom mobility to increase and to distribute the atoms more homogeneously. So, as shown in figure 7, the strain on Ge atoms increases linearly as the Ge concentration increases in the second group of samples just as reported for the Si–Ge alloy where the Ge atoms are distributed randomly and homogeneously [1–3]. The Si–Si Raman peak shifts to a low frequency and the Ge–Ge peak shifts to a high frequency as the temperature decreases (or the Ge concentration increases). So the abnormal results in figure 1 for the Ge–Ge Raman peak shift to a lower frequency when the Ge concentration is increased could become normal by increasing the substrate temperature. Even the FWHM of the Ge–Ge Raman peak becomes smaller as the temperature increases; the decrement in the FWHM against Ge concentration has reduced compared with the first group of samples. The reason why the strain on the Si atoms decreases as the Ge concentration increases on decreasing the substrate temperature in figure 8 is unknown.

On the basis of the model that Ge atoms are distributed homogeneously and randomly in Si–Ge alloys [1–3], we calculate the Si–Si and Ge–Ge Raman shifts for fully strained Si–Ge alloys. Figure 4 shows that the calculation results for the Ge–Ge Raman shift (for fully strained Si–Ge alloys) were consistent with the experimental results of the second group in figure 2 but were very different from those of the first group. The reasons why

there were great differences between the calculation results and the experimental results for the Si–Si Raman shift of the second group is unknown. The Si–Ge alloys of different Ge concentrations deposited at different substrate temperatures were nearly standard samples in which atoms are distributed homogeneously to a great degree.

Comparing these two groups of samples, we find that the quality of the low-Ge-concentration samples deposited at a high temperature is higher than those deposited at a low temperature. In the first group deposited at a low temperature, the high-Ge-concentration Si–Ge alloys were of relatively high quality (here we mean that the Ge atoms are distributed relatively homogeneously). So a high Ge concentration needs a relatively low substrate temperature to deposit high-quality Si–Ge alloys, but a low Ge concentration requires a high growth temperature during the deposition of the Si–Ge alloys.

4. Conclusion

In summary, Raman spectroscopy has been employed to investigate the microstructural features of the strained Si–Ge alloys. The Ge atoms in the high-Ge-concentration Si–Ge alloy are distributed more homogeneously and randomly than in the low-Ge-concentration Si–Ge alloy. The substrate temperature has a great influence on the microstructure of the strained Si–Ge alloys. The deposition of high-quality Si–Ge alloys of high Ge concentration requires a relatively low substrate temperature and the deposition of alloys with a low Ge concentration requires a relatively high substrate temperature.

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