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Effect of thermal annealing on the Raman spectrum of $Si_{1-x}Ge_x$ grown on Si

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The effect of thermal annealing on the Raman spectrum of $Si_{1-x}Ge_x$ grown on Si was investigated in the temperature range of 800–1100 °C on three samples having Ge contents x of 0.2 and thicknesses of 0.08, 0.16, and 0.40 μm. For annealing below 900 °C, the stress relaxation played an important role on the Raman shift. The degree of the stress relaxation in a dislocation free sample was smaller than that in a sample with partially relaxed stress. Stress was not completely relaxed in any of our samples after annealing. For annealing above 900 °C, diffusion strongly affected the Raman shift and the spectral lineshape. The critical thickness was close to 0.08 μm.

I. INTRODUCTION

Recently, heterostructures based on $Si_{1-x}Ge_x$ have attracted much interest because of its applications to heterobipolar transistors.[1] For this reason, it is important to investigate the effects of thermal annealing on these systems. The stability of heterostructures based on $Si_{1-x}Ge_x$ has been considered by many researchers[2–7] and is reviewed in Ref. 8. Timbrell *et al.*[6] showed a correlation between stress relaxation and dislocation generation using Raman scattering, x-ray double-crystal diffractometry (DCD), electron beam induced current (EBIC), and cross-sectional transmission electron microscopy (XTEM). They performed rapid thermal annealing (RTA) on a sample with an epitaxial layer thickness of 0.2 μm in the temperature range from 500 to 850 °C. Schorer *et al.*[7] investigated the structural stability of short-period Si/Ge superlattices in the temperature range of 430–780 °C. Here, we consider the effect of thermal annealing on a single $Si_{1-x}Ge_x$ layer on Si in the high temperature range of 800–1100 °C.

The purpose of this article is to study effects of thermal annealing on the Raman spectrum of $Si_{1-x}Ge_x$ on Si. Three different samples with Ge content $x=0.2$ were studied: a sample of thickness 0.08 μm which is dislocation free and fully strained (sample 1), a sample of thickness 0.16 μm in which stress is partially relaxed (sample 2), and a sample of thickness 0.40 μm in which stress is fully relaxed (sample 3). The magnitude of the stress relaxation is quantitatively estimated by Raman scattering. The annealing temperature was varied in a wide range between 800 and 1100 °C. The Raman shift is affected by both stress and diffusion. At annealing temperatures below 900 °C, the effect of diffusion can be neglected, and we find that the degree of the stress relaxation in sample 1 is smaller than that in sample 2. At annealing temperatures above 900 °C, the effect of diffusion cannot be neglected, and it becomes difficult to estimate quantitatively the magnitude of the stress relaxation. In our experiments, the critical thickness is close to that reported by Kohama *et al.*[4]

II. EXPERIMENTAL PROCEDURES

Samples were prepared as follows: The $Si_{1-x}Ge_x$ layer was grown at 620 °C on a 4-in.-diam Si wafer using very low pressure chemical vapor deposition (VLPCVD).[9,10] The thicknesses of samples with Ge content $x=0.2$ were varied from 0.08, 0.16, 0.40 to 0.80 μm by controlling the growth time while keeping the same gaseous conditions. The sample of thickness 0.80 μm was used only in the first experiment for confirming that a stress is fully relaxed in sample 3. At this stage, these samples referred to as "as-deposited samples," were annealed at 800, 900, 1000, and 1100 °C for 30 min. The process of increasing and decreasing the temperature for annealing took 3 min. The values of the thickness and the Ge content x were determined by secondary ion mass spectroscopy (SIMS) analysis. The thickness was also confirmed by the intensity ratio of the Si phonon mode from the $Si_{1-x}Ge_x$ layer to the Si substrate in the Raman spectrum. Raman spectra were measured at room temperature in a backscattering geometry by using a cw Ar^+ laser at 4880 Å. Scattered photons were analyzed with a SPEX double monochromator (Model 1401) equipped with an electrically cooled photomultiplier and a digital photon counting system. The focused laser spot size was about 0.2×2 mm^2.

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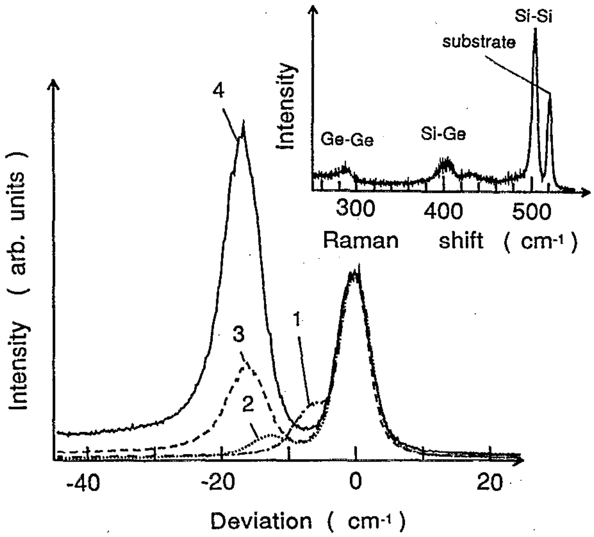

FIG. 1. Raman spectra of $Si_{1-x}Ge_x$ on Si as a function of layer thickness. (1) 0.08 μm (sample 1), (2) 0.16 μm (sample 2), (3) 0.40 μm (sample 3), and (4) 0.80 μm. The inset shows the spectrum in the range from 250 to 550 cm^{-1}.

III. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the $Si_{1-x}Ge_x$ samples. The Raman spectrum in the range from 250 to 550 cm^{-1} is shown in the inset of this figure. Two strong peaks appear at 521 and 505 cm^{-1}; these are due to the Si phonon modes of the substrate and of the $Si_{1-x}Ge_x$ layer, respectively. In Fig. 1, the signal is normalized by the peak from the substrate. Notice that the intensity from the $Si_{1-x}Ge_x$ layer decreases and its peak position changes with an increase in the layer thickness.

The peak position of the mode from the $Si_{1-x}Ge_x$ layer was obtained by fitting the spectra to a theoretical curve consisting of two Lorentzians. The results are shown in Fig. 2. The peak position monotonically decreases with an increase in the layer thickness. For the 0.40 μm- (sample 3) and 0.80-μm-thick samples, the positions have the same value of 505 cm^{-1}. Since this value is the same as that in the $Si_{1-x}Ge_x$ bulk crystal observed by Byra,[11] we conclude that the stress is totally relaxed in these layers. On the other hand, the 0.08-μm-thick sample (sample 1) was found to be dislocation free and fully strained using XTEM. Figure 2 confirms that the stress is partially relaxed in sample 2.

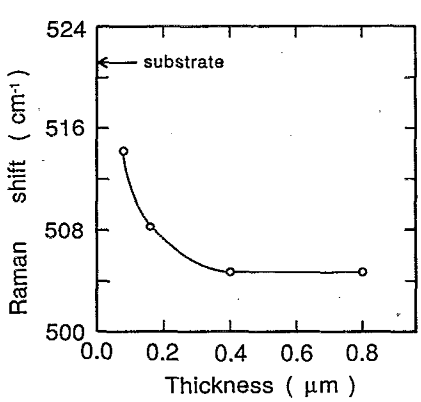

FIG. 2. Peak positions of the Si phonon mode in $Si_{1-x}Ge_x$ as a function of thickness. The peak position of the Si phonon mode of the substrate is indicated.

The Raman peak shift $\delta\omega$ is written as[6]

$$\delta\omega=(p/2\omega_0)\epsilon_\perp+(q/\omega_0)\epsilon_\parallel=b\epsilon=b(S_{11}+S_{12})\tau, \quad (1)$$

where p and q are phenomenological material parameters, ϵ is the strain, S_{11} and S_{12} are the alloy compliances, and τ is the built-in interfacial biaxial stress. By using data of the Raman peak shift for a stress for pure Si, 0.4 cm^{-1}/kbar,[12] we estimate that a stress of about 24 kbar is generated in the 0.08-μm-thick layer of sample 1. Since the peak shift is proportional to the stress in Eq. (1), the magnitude of the stress relaxation of the 0.16-μm-thick layer (sample 2) is calculated to be 36% according to the results shown in Fig. 2.

It is interesting to compare our result on the critical thickness with previously reported ones.[2–4] The critical thickness h_c is between 0.08 and 0.16 μm and is close to 0.08 μm (see Fig. 2). This value is close to 0.05–0.1 μm, as reported by Kohama *et al.*[4] and is much smaller than 0.3 μm, as reported by Bean *et al.*[2] and People and Bean.[3] Kohama *et al.*[4] measured the critical thickness using EBIC and TEM. These authors claimed that measurements of lattice distortion by x-ray diffraction and Rutherford backscattering techniques, which Bean *et al.*[2] and People and Bean[3] used, introduces erroneous results because the lattice distortion of $Si_{1-x}Ge_x$ is not relaxed at or over h_c. Our result supports their claim.

In Fig. 3, the spectra after thermal annealing at 900 and 1100 °C are shown. As a reference, the spectrum for the as-deposited sample is also shown. A shift of the peak from the $Si_{1-x}Ge_x$ layer was observed in the spectra of the 0.08 and 0.16 μm samples (samples 1 and 2, respectively) after thermal annealing at 900 and 1100 °C [see Figs. 3(a) and 3(b)]. The change in spectral shape is significant especially in the 0.16 and 0.40 μm samples after thermal annealing at 1100 °C [samples 2 and 3, respectively. See Figs. 3(b) and 3(c)]. The peak position of the Si phonon mode in $Si_{1-x}Ge_x$ is plotted as a function of the annealing temperature in Fig. 4 for the various layer thicknesses. There are two reasons why the epitaxial layer is affected by thermal annealing: (1) stress relaxation and (2) thermal diffusion. The diffusion length after thermal annealing at 900 °C for 30 min is estimated to be 40 Å based on the data by van de Walle *et al.*[5] This value is consistent with our SIMS results, and thermal diffusion can be neglected below 900 °C in our samples. Therefore, below 900 °C we can estimate the magnitude of the stress relaxation using the results in Fig. 4. The slopes of the curves in Fig. 4 below 900 °C are 5×10^{-3} kbar/°C in sample 1 (0.08 μm thick) and 1×10^{-2} kbar/°C in sample 2 (0.16 μm thick). Stress relaxes in sample 2 more readily than in sample 1 because there are dislocations in the former sample. It is interesting to note that the stress is not completely relaxed in either sample 1 or 2 after annealing at 900 °C.

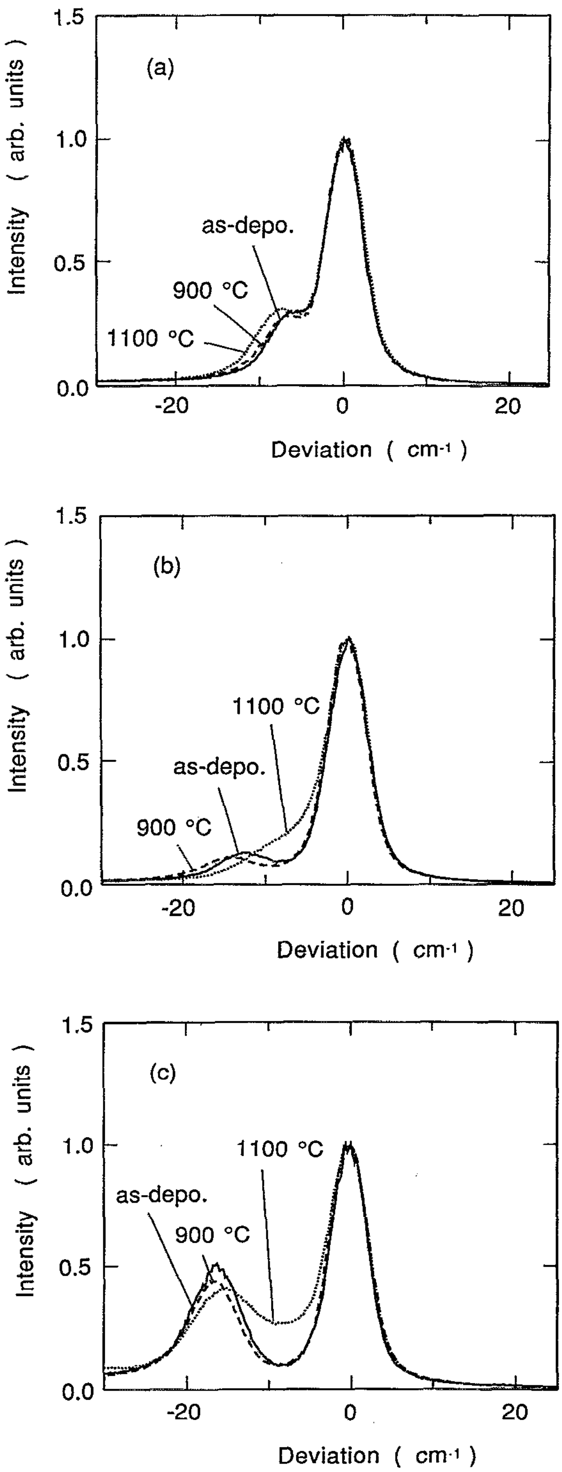

FIG. 3. Raman spectra before and after thermal annealing at 900 and 1000 °C for 30 min. (a) 0.08 μm (sample 1), (b) 0.16 μm (sample 2), and (c) 0.40 μm (sample 3).

Above 1000 °C, thermal diffusion affects the peak shift and the spectral shape [see Fig. 3(b) and 3(c)]. The peak position is mainly determined by the effective fraction of germanium after diffusion, and it is difficult to quantitatively estimate the stress relaxation. If the effective value of

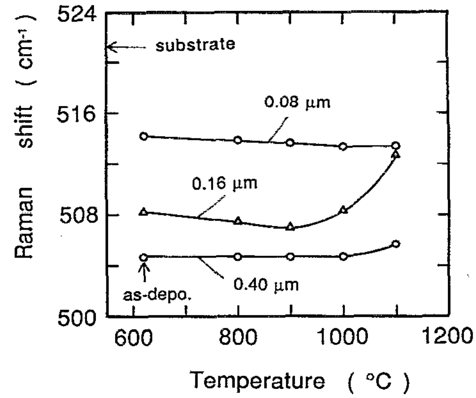

FIG. 4. Peak positions of the Si phonon mode in $Si_{1-x}Ge_x$ as a function of annealing temperature. The peak position of the Si phonon mode in the substrate is indicated.

Ge content x is about 0.1 at 1100 °C, the peak position of the $Si_{1-x}Ge_x$ bulk mode without stress is about 513 cm^{-1}. This explains the results of samples 1 and 2 in Fig. 4. The peak position in sample 3 at 1100 °C can be accounted for by an effective value x of about 0.19. It is important to note that thermal effects are limited to thermal diffusion in sample 3, since the stress is totally relaxed.

IV. CONCLUSIONS

We studied effects due to thermal annealing on the Raman spectra of $Si_{1-x}Ge_x$ grown on Si in the temperature range of 800–1100 °C. Three samples with Ge content x =0.2 and thicknesses 0.08, 0.16, and 0.40 μm were investigated. After annealing below 900 °C, the stress relaxation played an important role on the Raman shift. The degree of stress relaxation in a dislocation free sample was smaller than that in a sample with partially relaxed stress. In both these samples, the stress was not completely relaxed at 900 °C. After annealing above 1000 °C, diffusion strongly affected the Raman shift and the spectral shape. Unfortunately it is difficult to estimate the magnitude of the stress relaxation. In our experiments, the critical thickness was close to 0.08 μm, in agreement with the value reported by Kohama *et al.*[4]

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