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Micro-Raman Characterization of a Ge/Si Heterostructure Grown by Chemical Vapor Deposition

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SUMMARY A Ge/Si structure grown by chemical vapor deposition (CVD) is angle-lapped and characterized by the micro-Raman spectroscopy. Near the interface, the phonon mode due to the Si-Ge bond is clearly observed, which indicates that a SiGe alloy is formed by the solid-phase interdiffusion at the interface. The thickness of the interfacial alloy layer is about 0.2 μm . Amount of residual strain is estimated by comparing the measured phonon frequencies with those predicted from the composition profile, but the shift due to the residual strain is not appreciable. Both the interdiffusion at the interface and the nearly complete relaxation of the lattice mismatch are attributed to the high growth temperature of the CVD sample.

key words: Raman spectroscopy, heterostructure, Ge/Si, interdiffusion, lattice-mismatch

1. Introduction

In structural characterization of semiconductor heterostructures, the attention is usually focused on either of the following two points. (1) Strain and dislocations caused by the lattice mismatch between the layers. (2) Interdiffusion or mixing at the hetero-interface. These two points are related to each other: The interdiffusion may be accelerated by the strain^{(1),(2)}, and the lattice relaxation is influenced by the composition profile near the interface⁽³⁾. The strain can be accurately measured by X-ray diffraction (XRD), but the lattice constant obtained by XRD is an averaged one and the local strain near the interface is difficult to detect. Transmission electron microscope (TEM) observation can reveal dislocations, but it is not easy to determine amount of strain accurately by

TEM. In order to measure the profile of composition, secondary-ion-mass spectroscopy and Auger electron spectroscopy are frequently used, but crystalline quality cannot be deduced from results of these measurements.

Raman spectroscopy can in principle determine both alloy composition and strain simultaneously and thus is regarded as a powerful tool for characterizing the heterostructures. In this study, we use the Raman spectroscopy to characterize a Ge/Si heterostructure. SiGe/Si heterostructures have been extensively studied since they are indispensable for Si-based heterostructure devices, such as a heterojunction bipolar transistor⁽⁴⁾. Our samples were grown by chemical-vapor deposition (CVD). Although molecular-beam epitaxy (MBE) has begun to be widely used, CVD is still thought to be a useful method for obtaining high-quality materials. The quality of the grown layer depends critically on the crystalline structure near the heterointerface. In order to characterize the near-interface region, we bevel the sample and adopt micro-Raman spectroscopy: the laser beam is focused at the interface region which is exposed on the bevel formed by the angle lapping. Figure 1 shows a schematic of our experiment. So far, many Raman studies have been done on SiGe bulk alloys^{(5)–(8)} and SiGe/Si heterostructures^{(9)–(14)}, but the microscopic probe was used in only one of these studies⁽¹⁴⁾.

Details of the experimental procedure are described in the next section. The results are given in Sect. 3 and discussed in Sect. 4.

2. Experimental Procedure

The Ge heteroepitaxial layer was grown directly on a (100) Si substrate by low-pressure CVD using hydrides as source materials. The thickness of the Ge layer is 6 μm , the growth period 40 min, and the growth temperature 840°C. For comparison, Si_{1-x}Ge_x alloy layers with various alloy composition x were grown under similar conditions. The alloy composition was determined from the lattice constant measured by XRD. These alloy layers were not angle-lapped, and the Raman measurement of them was performed only on the as-grown surfaces.

The Ge/Si structure was angle-lapped using al-

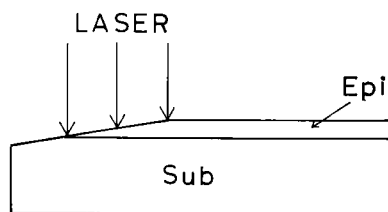


Fig. 1 Schematic of the micro-Raman experiment.

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mina powder of 1- μm grit size. After the lapping, we carried out a chemical etching using 1:1:10 HF:H₂O₂:H₂O solution to remove the damaged region. The etch depth is about 0.5 μm . The angle of the bevel was estimated to be about 0.75°⁽¹⁵⁾, but the actual angle after the etching may differ from it, as discussed in Sect. 4.

The Raman measurement was conducted using the 514.5 nm line of an Ar ion laser in a back scattering configuration. Diameter of the beam spot, which is focused by an optical microscope, is about 1 μm on the sample surface. Data were collected using a conventional photomultiplier. The spectral line width is 3 cm^{-1} and the accuracy of the determination of frequency shift $\pm 0.3 \text{ cm}^{-1}$.

3. Results

3.1 Si_{1-x}Ge_x Bulk Alloys

As will be shown in the next section, a Si_{1-x}Ge_x alloy is formed in the interface region of the Ge/Si structure. Thus, we investigate phonon properties of Si_{1-x}Ge_x bulk alloys in order to interpret data for the interface region of Ge/Si.

Figure 2 shows Raman spectra for Si_{1-x}Ge_x ($x=1, 0.76, 0.44$). The peaks near 300 cm^{-1} are due to the Ge-Ge bond, those near 400 cm^{-1} the Si-Ge bond, and those near 500 cm^{-1} the Si-Si bond. The peak frequencies of these three peaks are plotted in Fig. 3 as a

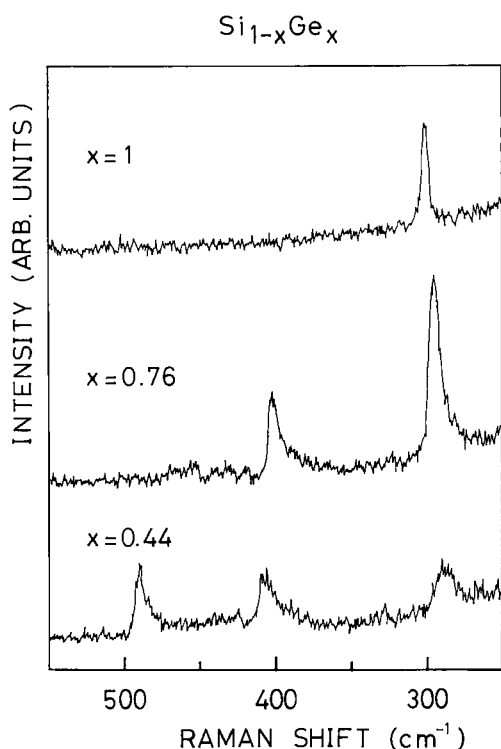


Fig. 2 Raman spectra for Si_{1-x}Ge_x alloys ($x=0.44, 0.76, 1$). They were measured on as-grown surfaces.

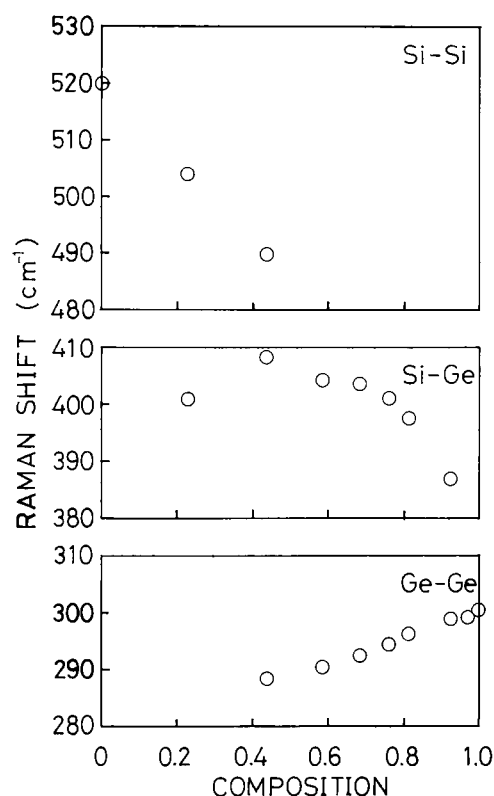


Fig. 3 Peak frequencies of three phonon modes in Si_{1-x}Ge_x as a function of composition x .

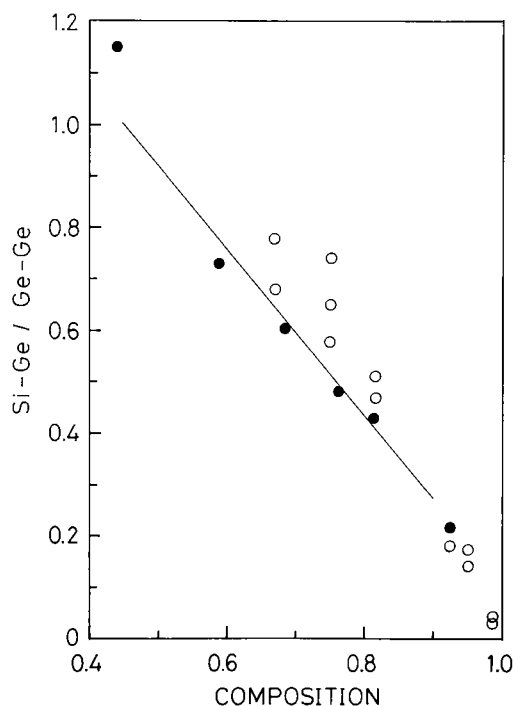


Fig. 4 Composition dependence of intensity ratio of the Si-Ge peak to the Ge-Ge peak. The dark circles: the present results. The open circles: taken from Ref.(5). The solid line is a straight line fitted to the data shown by the dark circles.

function of composition x . The Ge-Ge peak frequency has nearly linear dependence on composition and is approximately expressed by the equation

$$\omega_{\text{Ge-Ge}} = 301 - 23(1 - x) \quad (\text{cm}^{-1}) \quad (1)$$

for x larger than 0.4. These results agree with previously reported data⁽⁶⁾.

The $\text{Si}_{1-x}\text{Ge}_x$ layers characterized here were grown on Si substrates and thus are not truly bulk materials. However, the thickness of the layer is larger than $5 \mu\text{m}$, and thus the layers are expected to be fully relaxed near the as-grown surface. Therefore, they can be regarded as a bulk material in the Raman measurement, since the penetration depth of the laser beam is less than $1 \mu\text{m}$.

Figure 4 shows intensity ratio of the Si-Ge peak to the Ge-Ge peak as a function of x . The dark circles show the results of the present study, and the data represented by the open circles are taken from Ref. (5). Both agree qualitatively. In the composition range between 0.44 and 0.9, the data shown by the dark circles can be fitted as a first approximation by the equation

$$r = 1.64(1 - x) + 0.11 \quad (2)$$

where r is the intensity ratio. If the intensity of each peak is proportional to number of the corresponding bond, r should be proportional to $(1 - x)/x$. However, the actual ratio deviates from this relation, especially

for $x < 0.7$.

3.2 The Ge/Si Structure

Figure 5 shows Raman spectra at three distinct positions on the bevel of the angle-lapped Ge/Si sample. d is the distance from (normal to) the interface. (The composition profile is not abrupt, and thus we cannot rigorously determine the position of the interface. Here, we define the "interface" as the position where a Raman signal other than that for pure Si begins to appear.) The sharp peak at 520 cm^{-1} is due to the Si substrate (pure Si), and its intensity decreases with distance from the interface. In addition to the signal of the substrate, three peaks appear near the interface, and they obviously correspond to the peaks observed in the $\text{Si}_{1-x}\text{Ge}_x$ alloys. This clearly shows that a $\text{Si}_{1-x}\text{Ge}_x$ alloy is formed at the interface.

Near the interface, the Ge-Ge peak is broad and asymmetric with tailing toward lower wavenumbers. This will be mainly due to compositional disorder in the interfacial alloy layer and not due to structural defects, since the thick alloy layers also exhibit similar broadening as shown in Fig. 2. However, composition variation along the growth direction may cause further broadening because the penetration depth of the laser

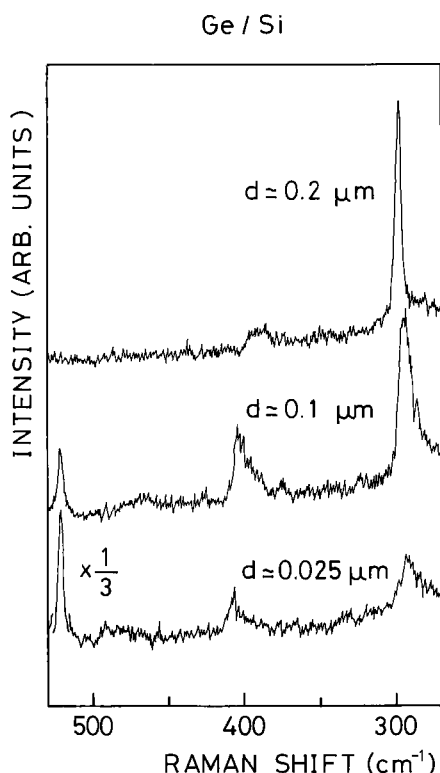


Fig. 5 Raman spectra at various positions in the Ge/Si structure. d is distance from the interface.

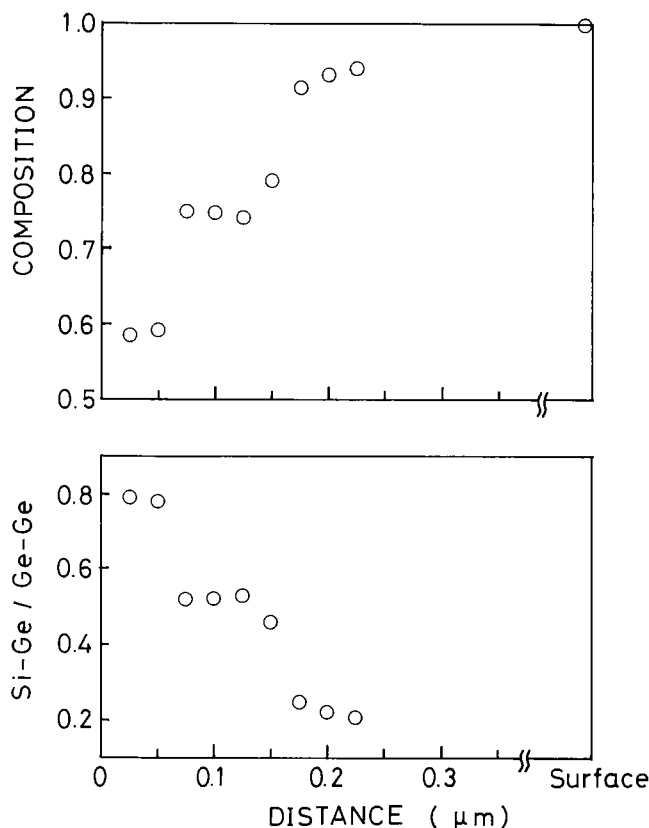


Fig. 6 Intensity ratio of the Si-Ge peak to the Ge-Ge peak and composition x deduced from it as a function of distance from the interface in the Ge/Si structure.

beam is finite. The influence of the finite penetration depth is discussed in Sect. 4. 3, too.

The residual strain may exist near the interface, and the strain causes shift in the Raman frequency. The strain might also affect the Raman intensity, although the dependence of the intensity on the strain has not been investigated. However, it is not likely that the change in the Si-Ge intensity due to the strain is significantly different from that in the Ge-Ge intensity. Therefore, the alloy composition can be deduced from the intensity ratio r using Eq.(2) even if the residual strain remains. Figure 6 shows the depth profile of r and composition x deduced from r . According to this result, the composition changes gradually at the interface, and the thickness of the transition layer is about $0.2\ \mu\text{m}$. (In the figure, Ge composition at the "interface" is 0.58. In fact, it will decrease gradually to null in the region of $d < 0$, but we cannot observe the Raman signal of the alloy there because of the limited sensitivity of our system.)

Figure 7 shows frequencies of the Ge-Ge and Si-Ge peaks as a function of the distance from the interface. The shift in the frequency is caused by both the composition change and the strain. In the next section, we attempt to distinguish between these two effects.

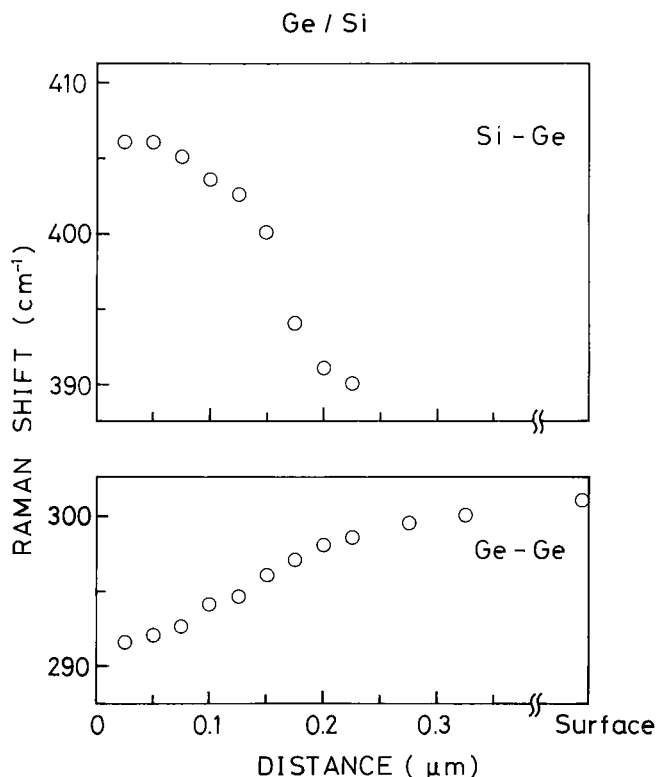


Fig. 7 Profiles of the peak frequencies of the Si-Ge and Ge-Ge peaks in the Ge/Si structure.

4. Discussion

4. 1 Interdiffusion

As shown in the previous section, the $\text{Si}_{1-x}\text{Ge}_x$ alloy is formed at the interface of the Ge/Si structure. The alloy is not formed by mixing in the gas phase: in the growth of Ge/Si, the Ge layer was grown directly on Si without a buffer layer, and thus silane was not introduced into the growth chamber. Therefore, the alloy is formed by interdiffusion in the solid phase. The interdiffusion of Si and Ge atoms has been studied for superlattice structures, and the interdiffusion coefficient D was estimated to be about $1 \times 10^{-17}\ \text{cm}^2\text{s}^{-1}$ at 840°C , the growth temperature of our samples^{(13),(16)}. Then, the approximate diffusion length $2\sqrt{Dt}$ is about 3 nm, if t is thought to be the growth interval (40 min). However, the thickness of the alloy layer is $0.2\ \mu\text{m}$, much larger than the expected diffusion length. Thus, the actual diffusion coefficient seems more than three orders of magnitude larger than the reported value. The samples of the previous studies were superlattices consisting of Si and $\text{Si}_{1-x}\text{Ge}_x$, whereas our sample consists of pure Si and Ge. Hollander reported that the diffusion coefficient increases with Ge content of the alloy layers⁽¹⁶⁾. Therefore, the difference in the value of D is mainly due to the difference in composition of the layers. However, the difference may be

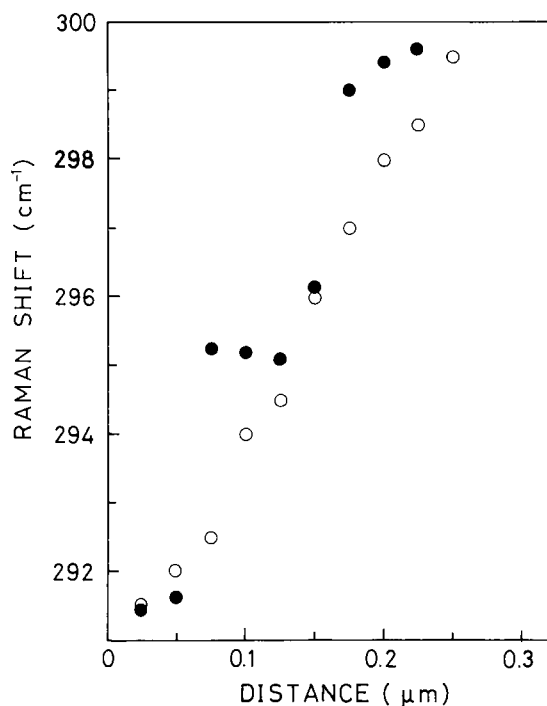


Fig. 8 Comparison between the measured Ge-Ge peak frequencies and those predicted from the composition profile shown in Fig. 6.

exaggerated because of error in estimate of the distance from the interface, as discussed in Sect. 4. 3.

4. 2 Strain

The peak frequency may be shifted by residual strain near the interface. Here, we concentrate our attention on the Ge-Ge peak, since its peak frequency can be accurately determined owing to its small width.

The peak frequency is influenced by both strain and alloy composition. The composition profile has been determined from the intensity ratio r , as shown in Fig. 6. We have also measured the relation between the peak frequency and the composition for the unstrained materials (Fig. 3). Then, assuming the absence of the residual strain, we can predict the profile of the peak frequency from the composition profile on the basis of the results shown in Fig. 3. If there is no residual strain, the frequency profile thus predicted should coincide with the measured profile. The dark circles in Fig. 8 represent the predicted profile and the open circles the measured one. Although there is rather large scatter in the data, especially in those shown by the dark circles, it can be seen from the figure that the measured frequencies are nearly equal to or slightly lower than the predicted ones. If the strain due to the lattice mismatch remains near the interface, the Ge layer would be compressed because of its larger lattice constant and the measured frequency would become higher than the predicted one. Therefore, the present results indicate that there is no appreciable misfit strain near the interface in the Ge/Si structure.

The difference in thermal expansion coefficient between Ge and Si causes tensile stress in the Ge layer. Thus, the residual strain, if exists, would be due to the thermal stress. However, it seems difficult to deduce the amount of the strain quantitatively because of large scatter in the data.

In the previous studies, we characterized GaAs/InAs, InGaAs/InAs, and InGaAs/GaAs structures by the same method as in this study and found appreciable residual misfit strain near the interface^{(15),(17)}. For example, the frequency shift due to the residual strain is 3 cm^{-1} in the vicinity of the interface of the GaAs/InAs structure. Chang et al. measured Raman spectra near the interface between a SiGe/Si superlattice and a Si substrate using the same method as ours, and found a positive shift of about 2 cm^{-1} caused by the mismatch stress⁽¹⁴⁾. Thus, the relaxation of the misfit stress is more complete in the CVD Ge/Si structure than in the samples of the previous studies. This will be mainly due to the high growth temperature of the CVD sample. The samples of the previous studies were grown by MBE at about 500°C , a temperature much lower than the growth temperature of the present sample (840°C). At low temperatures, the movement of dislocations is hindered, and thus the relaxation is not

accomplished. Relevant results have been reported by Kvam and Namavar⁽¹⁸⁾. They investigated the lattice relaxation in SiGe/Si structures grown by CVD and concluded that the threading dislocation density is smaller in the CVD SiGe/Si than in MBE SiGe/Si because of fast dislocation movement at CVD growth temperature.

4. 3 Error in the Depth Profiling

In this subsection, we discuss two factors causing error in estimate of the distance from the interface.

In the previous study, we estimated the bevel angle to be 0.75° ⁽¹⁵⁾. The Ge/Si sample was lapped using the same tool, and thus the angle would be 0.75° before the etching. However, it may be different after the etching because of the dependence of the etch rate on the alloy composition. As shown in Fig. 6, the composition changes gradually near the interface, and accordingly, the etch rate also changes there. The etch rate is smaller in a more Si-rich region, and thus the angle may become smaller after the etching. This leads to overestimate of the distance from the interface in the profiling.

In addition, the measured profile may deviate from the actual one because of the finite penetration depth of the laser beam. In the Raman measurement, we observe a spectrum averaged within a region of a thickness of $(2\alpha)^{-1}$, where α is the absorption coefficient for the laser beam. $(2\alpha)^{-1}$ of Ge is very small, about 10 nm for the 514.5 nm line. Thus, the penetration of the beam does not cause significant error for the Ge layer. However, α is smaller in $\text{Si}_{1-x}\text{Ge}_x$ alloys. Although the value of α of the alloy is not accurately known, we can expect that $(2\alpha)^{-1}$ of $\text{Si}_{0.4}\text{Ge}_{0.6}$, for example, is several times larger than that of Ge because the E_1 energy of $\text{Si}_{0.4}\text{Ge}_{0.6}$ is 2.5 eV⁽¹⁹⁾, larger than the photon energy (2.41 eV). Therefore, the error due to the penetration of the laser beam may be significant in the close vicinity of the interface, where the Si content is relatively large.

The two factors discussed here make the observed profile more gradual than the actual one, and thus the thickness of the transition layer will be overestimated in our profiling.

5. Conclusion

We have characterized a CVD Ge/Si structure by the micro-Raman spectroscopy. The sample was angle-lapped so that the interface region is exposed on the bevel. Near the interface, the phonon mode due to the Si-Ge bond was clearly observed. The profile of the alloy composition was obtained from the intensity ratio of the Si-Ge mode to the Ge-Ge mode. The composition changes gradually at the interface, and the thickness of the transition layer is about $0.2\text{ }\mu\text{m}$. The measured phonon frequencies and those predicted

from the composition profile are identical within the experimental uncertainty. This indicates that the misfit stress is relaxed nearly completely. The interdiffusion at the interface and the nearly complete relaxation of the lattice mismatch are attributed to the high growth temperature of the CVD sample.

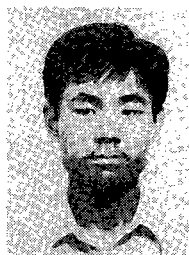
The growth temperature of MBE is usually much lower than that of CVD. Thus, it is interesting to compare Ge/Si structures grown by MBE and CVD. For further study, the same characterization method will be applied to Ge/Si structures grown by MBE.

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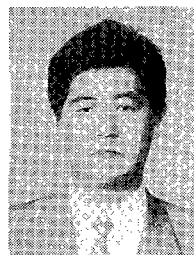
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