Raman study of strain relaxation in Ge on Si

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Strain in thin Ge layers grown by molecular beam epitaxy on (100) Si is measured by a Raman technique. When the average Ge thickness is 7 monoatomic layers (ML), Raman results show that the layer is almost coherent to the Si lattice. The strain begins to decrease at an average thickness of 10 ML, i.e., the critical thickness of dislocation generation is 10 ML. On the other hand, the relaxation begins at a thickness of 5 ML, according to reflection high-energy electron diffraction observation during the growth. This initial stage relaxation is due to deformation of islands and not due to dislocation formation. Raman results for thicker layers show that with increasing layer thickness, the misfit strain decreases gradually but more rapidly than predicted by the theory of Matthews and Blakeslee [J. Cryst. Growth **27**, 118 (1994)]. © *1995 American Institute of Physics.*

I. INTRODUCTION

In a lattice-mismatched heteroepitaxy, mismatch strain greatly influences the crystal growth mechanism, causing a morphological change and a defect generation. In Ge growth on a Si substrate, these phenomena take place in a very early stage because the lattice mismatch between Si and Ge is large (4%). So far, the initial stage of the growth has been investigated by reflection high-energy electron diffraction (RHEED) measurements during the molecular-beam epitaxial (MBE) growth.[1,2] The reported RHEED results for the Ge growth on (100) Si can be summarized as follows: (1) When the Ge layer thickness d is less than 5 monoatomic layers (ML), the layer grows two dimensionally. The surface lattice constant is equal to that of bulk Si, i.e., the layer is coherently strained. (2) For $d>5$ ML, islands of Ge atoms are formed on the complete layer already grown (Stranski–Krastanov type growth). When d is in the range of 5–10 ML, dominant facets of the islands are (811) planes. The surface lattice constant of the islands deviates from that of the substrate by about 2%, i.e., the Ge lattice constant returns halfway back to its bulk value. (3) When $d>10$ ML, the dominant facets become (311) planes. The surface lattice constant is close to the Ge bulk value.

Although the observation of the growth by RHEED was thus successful, the growth mechanism of Ge on Si has not been well understood. There seems to be no satisfactory explanation of the fact that the relaxation occurs by two stages. It is obvious from the above results that there is a close correlation between the morphological change and the strain relaxation, but this fact can in principle be explained in two different ways: (1) the formation of islands leads to relaxation of the surface lattice owing to the elastic deformation of the islands.[3] (2) Ge atoms gather at a position where the strain is relaxed by the misfit dislocations, and they form an island there.[4] At present, it seems unclear which mechanism is operative in each relaxation stage. Both macroscopic islands (~25 nm high) and microscopic islands (~3 nm high) have been observed by scanning tunneling microscopy,[5] and the relaxation mechanism may depend on the island size. In

addition, the growth mechanism might be further complicated by the intermixing of Ge and Si. In fact, a research group claimed that a concentrated $Si_{1-x}Ge_x$ alloy with an ordered structure is formed in the early stage of Ge growth on Si.[6]

The strain relaxation in a later stage (in a thicker layer) has not been clarified, either. There is no physical ground to believe that the relaxation is completed in an instant. Rather, it will gradually reach completion with increase of the layer thickness. However, this gradual relaxation process has seldom been investigated.

In this study, we characterize thin Ge layers on (100) Si substrates by Raman spectroscopy. Whereas the lattice spacing of the surface is measured by RHEED, the average strain within the layer can be detected by the Raman method for layers with thicknesses much smaller than the penetration depth of the laser beam. In addition, we can also obtain chemical information from Raman measurements, since impurities such as Si in Ge have their own impurity modes. Therefore, the Raman spectroscopy and RHEED are complementary, and we can discuss the strain relaxation mechanism in detail by comparing results of these two characterizations. To our knowledge, such a comparative study has never been done before.

II. EXPERIMENTAL PROCEDURE

The Ge layers were grown by MBE at 515 °C. The (100) Si substrates were used and a homoepitaxial Si layer was grown as a buffer layer before the Ge growth. We prepared ultrathin Ge layers with four different thicknesses (7, 10, 13, and 20 ML). Since the layers are not a flat two-dimensional layer, the thickness is an average value calculated from the deposition rate and the growth interval. The surface morphology and the surface lattice constant were observed during the growth by RHEED. An about 10-nm-thick amorphous Si cap was deposited on the ultrathin Ge layers to protect them from air. 10-nm-thick and 1-μm-thick Ge layers were also grown under the same condition.

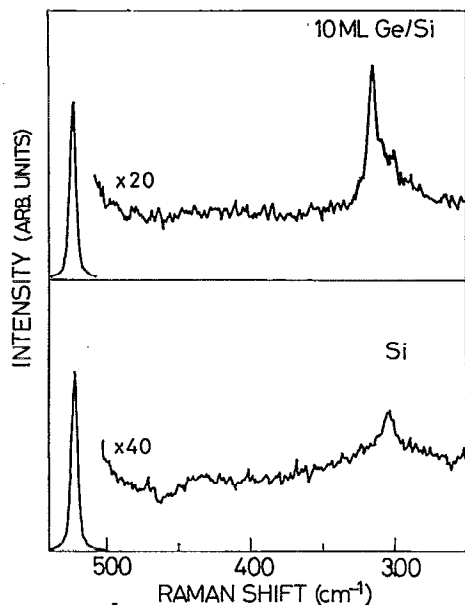© 1995 American Institute of Physics

FIG. 1. Raman spectra of the 10 ML Ge/Si structure and pure Si. The peak at 305 cm^{-1} in the spectrum for pure Si is due to the 2TA scattering.

FIG. 2. Raman spectra for the Ge layers on (100) Si after the subtraction of the pure Si spectrum. The layer thickness is shown in the figure.

The Raman measurement was performed using the 514.5 nm line of an Ar ion laser. The probe depth for Ge is about 10 nm, and thus the laser penetrates the whole layer except for the 1-μm-thick layer. For the 1-μm-thick layer, we also performed a micro-Raman measurement after forming a bevel to characterize the interface region. The scattered light was analyzed by a double monochromator and detected by a conventional photomultiplier. The spectral resolution is 3 cm^{-1} and the accuracy of determination of the frequency is ±0.3 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Relaxation in ultrathin layers

Figure 1 shows Raman spectra for pure Si and the 10-ML-thick Ge/Si structure. The second-order scattering of the transverse acoustic (TA) mode in Si appears at 305 cm^{-1}, near the frequency of the zone-center optical phonon in Ge. Since the Ge thickness is very small, the Raman signal of the 2TA scattering has a comparable intensity with the first-order Ge scattering. Thus, we subtracted the spectrum of pure Si from the spectra of the Ge/Si structures to accurately detect the Raman scattering of Ge. The subtraction was optimized by minimizing the intensity of the first-order scattering peak of the Si optical phonon in the difference spectra.

Figure 2 shows spectra of the ultrathin Ge layers after the subtraction. For comparison, the spectrum of the 1-μm-thick Ge layer is also shown. We found no appreciable strain in the 1-μm-thick Ge layer by the x-ray diffraction, and thus the peak frequency of the thick layer is expected to coincide with that of unstrained bulk Ge. As shown in the Fig. 2, the phonon frequencies in the thin Ge layers are positively shifted compared with that in the thick layer.

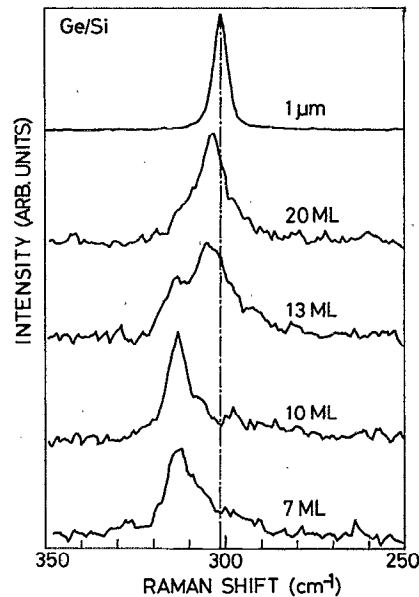It is well known that a positive shift in the vibration frequency is caused by compressive strain. The misfit strain is compressive for Ge, since the lattice constant of Ge is larger than that of Si. Thus, the above results show that the misfit strain remains in the Ge layers. The relation between the strain e and the shift $\Delta\omega$ is given by

$$e = 0.25\Delta\omega(\%) \tag{1}$$

for misfit strain in Ge layers on (100) substrates.[7] It should be noted that $\Delta\omega$ is the shift due to strain, which is not necessarily equal to the observed shift from the bulk frequency: the frequency shift is caused not only by strain but also by phonon localization, and thus the observed shift is in general the sum of both the contributions. In the present case, the localization of phonons along the growth direction necessarily occurs because the layer is very thin, and it will cause a downshift from the bulk frequency. Thus, we should know the shift due to the localization to obtain true values of $\Delta\omega$.

We adopted the linear-chain model to calculate the Raman spectra due to phonons localized in Ge layers on Si substrates. The linear-chain model has been successfully used to calculate vibration frequencies of semiconductor superlattices.[8,9] To simulate the n-ML-thick Ge/Si structure, we considered a chain composed of n Ge atoms and 150 Si atoms. The latter part is thought to simulate the Si substrate. The eigenvectors and frequencies of the vibrational modes were obtained by diagonalizing a matrix describing the motion of the $n+150$ atom chain. Only the nearest-neighbor interaction was taken into account, and the force constants were chosen so that the zone-center optical frequency of the infinite chain coincides with that of the respective bulk crystal. We used two different boundary conditions in the calculation, namely, a free-surface boundary condition and a fixed-surface boundary condition. In the actual samples, the surface is covered with amorphous Si. This will correspond to an intermediate case between these two conditions. The

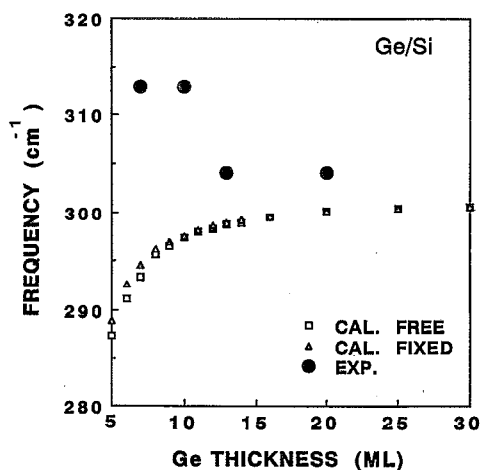J. Appl. Phys., Vol. 77, No. 10, 15 May 1995

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FIG. 3. Calculated and measured peak frequencies for Ge on Si. The squares represent frequencies calculated under the free-surface boundary condition and the triangles those calculated under the fixed-surface boundary condition. The strain is not taken into account in the calculation, and thus the difference between the calculated and measured values corresponds to the shift due to the strain.
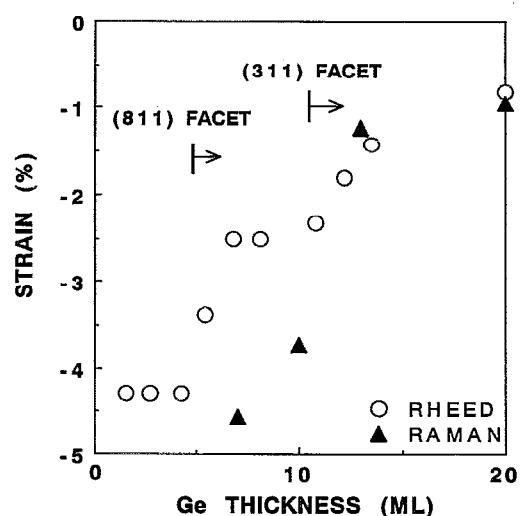

FIG. 4. Compressive strain in the Ge layers on Si as a function of the thickness. Dark triangles: obtained from the Raman spectra. Open circles: calculated from the surface lattice constant measured by RHEED.

Raman scattering efficiency of each mode was calculated by the bond-polarizability model,[8] and the Raman spectra were generated considering the natural linewidth, the instrumental resolution, and the Bose factor. Figure 3 shows peak frequencies of the calculated Raman spectra with the experimental peak frequency as a function of the layer thickness. The squares and the triangles represent frequencies calculated assuming a free boundary and a fixed boundary, respectively. The strain is not taken into account in the calculation. Therefore, the difference between the observed peak frequency and the calculated frequency is thought to correspond to the shift due to strain $\Delta\omega$, and the strain e is calculated from it using Eq. (1). For thicknesses concerned here, the difference due to the boundary condition is small, and we use an arithmetic mean of the two theoretical values in calculating $\Delta\omega$. It should be noted that although flat layers are assumed in this analysis, the actual films are islanded. Since the effect of the localization will be weak at the islands, where the thickness is locally larger than the average, this analysis may overestimate the negative shift due to the limited film thickness. This will lead to an overestimate of the compressive strain. On the other hand, if we compare the measured frequency with that of the bulk Ge, i.e., if we neglect the effect of the localization, the shift due to the strain is obviously underestimated.

The compressive strain thus obtained from the Raman spectra is shown by the dark triangles in Fig. 4 as a function of the Ge thickness. For comparison, the strain calculated from the surface lattice constant measured by RHEED is also shown by the open circles.

According to the RHEED results, the relaxation in the Ge layers on Si occurs by two stages. The first-stage relaxation occurs at a thickness of 5 ML: the strain is about 2.5% for thicknesses between 5 and 10 ML. On the other hand, the strain obtained from the Raman spectra is about 4% for thicknesses of 7 and 10 ML, i.e., the Raman results show that

the Ge layer is still strained almost coherently in this stage. As noted above, these strain values may be overestimated, but, even if we compare the measured frequency with that of the bulk Ge, the strain is still larger than 3%. Thus, there is a distinct difference between the Raman and the RHEED results. This indicates that the first-stage relaxation occurs mainly in the surface region and not in the inner region of the layer. Such relaxation will be attributed to deformation of the islands:[3,10] the lattice expands in the upper part of the island, where the constraint due to the substrate lattice is relatively weak, and thus the strain at the surface is smaller than the average strain in the whole island. This also explains why the first-stage relaxation and the island formation occur simultaneously.

The strain measured by RHEED is constant in the thickness range between 5 and 10 ML. This can also be explained considering that the relaxation in this stage is due to the island deformation. The RHEED results show that (811) planes remain the dominant facet in this stage, i.e., the shape of the islands (the ratio of the height to the width) remains unchanged in spite of the increase of the layer thickness from 5 to 10 ML. Therefore, the degree of the island deformation and thus that of the strain relaxation also remain unchanged.

For thicknesses larger than 10 ML, the Raman and RHEED analyses give essentially identical results: the strain is decreased to about 1%. This clearly shows that the relaxation of the second stage is different from the first-stage relaxation. We attribute the second-stage relaxation to misfit dislocation formation. If the misfit dislocations are formed at the Ge/Si interface, the strain is relaxed in the main body of the islands. Thus, the relaxed lattice is observed by both the RHEED and Raman techniques. When the strain is relaxed by the dislocations, strain energy in the island regions decreases further compared with the flat two-dimensional region, which is still coherently strained. Then, the tendency of Ge clustering in the island region will become stronger. This would lead to formation of the more slanting (311) facets.

At a thickness of 13 ML, the frequency of the dominant peak is 303 cm^{-1}, but another peak seems to appear at a frequency of 313 cm^{-1}. This indicates that the relaxation is not homogeneous. The relaxation will occur earlier in a larger or higher island. Thus, the inhomogeneous lattice relaxation will be due to inhomogeneous distribution of the island size. We observed a similar double-peak structure for some other 10 ML Ge/Si samples, too, although the higher frequency peak is more intense. Thus, the reproducibility is poor for the 10-ML-thick layer: we observed only a strained lattice as shown in Fig. 2 for some samples and observed a relaxed part as well for the other samples. For other thicknesses, the experimental results were well reproduced when we repeated the growth and the Raman experiments. This indicates that the thickness of 10 ML is just the critical thickness of misfit dislocation generation.

We did not measure the actual island size of the samples, and thus we cannot discuss the relation between the island size and the relaxation mechanism. Recently, it was reported that the island size tends to increase with growth temperature.[11] Since the relaxation is expected to start earlier for a larger island, the effective critical thickness may decrease with increasing growth temperature.

Ohshima et al. claimed that a concentrated $Si_{1-x}Ge_x$ alloy with an ordered atomic arrangement is formed in about 1-nm-thick Ge on Si.[6] They drew this conclusion from RHEED patterns having fractional order streaks. However, our Raman results exclude the possibility of the formation of concentrated alloys. If an alloy of $x=0.5$, for example, had been formed, we should have observed a scattering due to Si—Ge bonds near 400 cm^{-1} with intensity comparable to the Ge peak in the Raman spectra. However, such signal is absent in the spectra, as shown in Fig. 1. Considering the sensitivity of our measurement system, it can be concluded that even if an alloy layer exists, it should be dilute (with Si content smaller than 0.1) and/or very thin (1 or 2 ML). Therefore, the RHEED patterns observed in Ref. 6 cannot be attributed to the ordering and need another interpretation.

Tsang et al. have reported Raman spectra of ultrathin Ge layers on Si.[12] They observed null shift in frequency for the 5–6-ML-thick Ge layer. The Si cap layers in their samples were grown at high temperatures and thus significant intermixing would occur because of the segregation of Ge. This may cause a large downshift and make the apparent shift negligible in their data.

B. Relaxation in thicker layers

Figure 5 shows strain in the Ge layers as a function of the thickness. The average strain in the 1-μm-thick layer was found to be null by the x-ray diffraction measurement. The strain in the 10-nm-thick layer was determined from Raman data using Eq. (1); the probe depth is about 10 nm for Ge in the Raman measurement and thus the average strain was measured. As shown in Fig. 5, the amount of the compressive strain is about 0.5% for the 10-nm-thick Ge.

The solid curve in Fig. 5 is strain in the layer calculated on the basis of the equilibrium theory of the relaxation. The equilibrium strain is given by
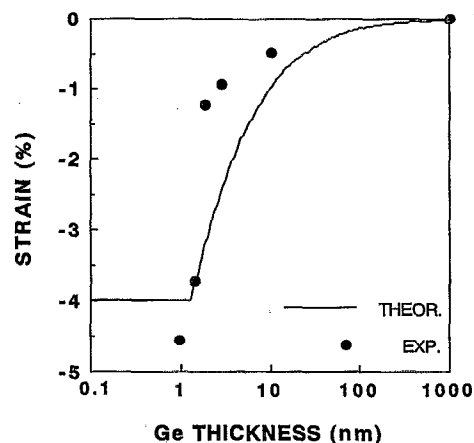

FIG. 5. Comparison of strain in Ge obtained from the Raman results (the dark circles) with theoretical results based on the model of Matthews and Blakeslee (the solid line).

$$e = \frac{a}{4\sqrt{2}\pi d} \frac{1-0.25\nu}{1+\nu}\left(1 + \ln\frac{\sqrt{2}d}{a}\right), \qquad (2)$$

where d is the layer thickness, a the lattice constant, and ν the Poisson ratio.[13,4] This equation is often used to calculate the critical thickness h_c, i.e., the thickness of onset of the relaxation, but the same equation can also be used to calculate residual strain in layers with thicknesses larger than h_c. The value of h_c calculated from the above equation is 1.3 nm, agrees well with the experimentally determined value, 10 ML (1.4 nm). However, the calculated residual strain is about two times larger than the experimental values for thicknesses larger than 10 ML. We can consider the following reasons for this disagreement: (1) A flat two-dimensional layer is assumed in the theory, but the actual layer has an island structure. The island formation may promote the relaxation. (2) The misfit dislocation is assumed to be a 60° perfect dislocation in deriving the above equation, but other types of dislocation may also be introduced. An edge dislocation is more effective in relaxing the strain than a 60° dislocation, and thus the strain will be reduced further when edge dislocations are introduced by pairing of two 60° dislocations and/or at the island edge. If the edge dislocation is assumed in deriving the equilibrium condition, $1-0.25\nu$ in Eq. (2) is replaced by 0.5. Thus, the equilibrium residual strain becomes about half of that shown by the solid line in Fig. 5.

For $Si_{1-x}Ge_x$/Si ($x<0.5$) structures, it has been reported that the relaxation is slower than prediction of the equilibrium theory, probably because of kinetic barriers to the dislocation formation.[14] This is in contrast with the results for $x=1$ shown in Fig. 5. This difference will be due to the difference in the misfit degree. When the misfit degree is not large, the layer grows two dimensionally. In addition, the interaction between dislocations is not significant because the spacing between the dislocations is relatively large. Then the theory may correctly predict the amount of the strain in the equilibrium state. Since there are in fact kinetic barriers
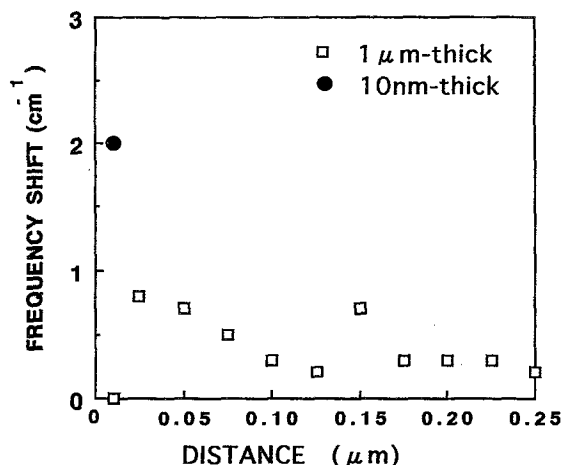
FIG. 6. Shift of the Ge Raman peak from the frequency at the surface of the 1-μm-thick Ge layer. The open squares: measured on the bevel formed on the 1-μm-thick Ge/Si sample using the micro-Raman technique. The dark circles: measured for the 10-nm-thick Ge layer on Si. The abscissa is the distance from the Ge/Si interface plane.

to the dislocation motion in semiconductors, it is natural that the actual strain value is larger than the equilibrium value.

In a thick heteroepitaxial layer, the strain distribution may be nonuniform along the growth direction. In order to observe the strain distribution in the 1-μm-thick layer, we angle lapped the sample and measured Raman spectra near the interface exposed on the bevel.[15] The obtained depth profile of the Ge peak frequency is shown by the squares in Fig. 6. The values of the frequency shift plotted here are shifts from the frequency at the surface of the 1-μm-thick layer. The abscissa is the distance from (normal to) the interface plane. Figure 6 shows that small positive shifts and thus small compressive (misfit) strain are observed near the interface of the 1-μm-thick Ge/Si.

From the intensity ratio of the Ge peak to the Si peak, the distance from the interface is estimated to be about 10 nm for the first point of the profile. As shown in the figure, the shift is null there. On the other hand, the peak shift of 2 cm^{-1} is observed for the 10-nm-thick Ge, as represented by the dark circles in Fig. 6. Thus, the peak frequency in the first 10-nm-thick region decreased by 2 cm^{-1} while the layer was growing to be 1 μm thick. This indicates that misfit dislocations were introduced within the first 10-nm-thick region during the growth of the thick layer.

IV. SUMMARY

We have measured strain in Ge layers on (100) Si by Raman spectroscopy. When the Ge thickness is 7 and 10 ML, the layer is partly relaxed according to the RHEED results but is almost coherent to Si according to the Raman analysis. For thicknesses larger than 10 ML, both techniques give an identical result that the mismatch strain is significantly relaxed. This indicates that the relaxation occurs first by deformation of the islands and next by dislocation formation. Results for thicker layers show that the relaxation due to the dislocation proceeds gradually with increasing layer thickness. The strain in a 10-nm-thick layer is about 0.5%, which is still large considering influences on material properties but significantly smaller than that expected from the widely accepted theory of the relaxation.

ACKNOWLEDGMENTS

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