

Elimination of misfit dislocations in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures by limited-area molecular-beam epitaxial growth

A. Nishida, K. Nakagawa, E. Murakami, and M. Miyao
Central Research Lab., Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

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Limited-area molecular-beam epitaxial growth of $\text{Si}_{1-x}\text{Ge}_x$ films, on a Si substrate with patterned SiO_2 , has been studied in order to eliminate misfit dislocations in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures. This method is found to dramatically reduce misfit dislocations in $\text{Si}_{1-x}\text{Ge}_x$ films. Hence, a thicker $\text{Si}_{1-x}\text{Ge}_x$ film can be grown, without introducing misfit dislocations, on a Si substrate with patterned SiO_2 than on a Si substrate without patterned SiO_2 . This phenomenon is attributed to the blocking of misfit dislocation extension and to a partial relaxation of the residual strain in the boundary between the crystal and polycrystalline $\text{Si}_{1-x}\text{Ge}_x$ film.

I. INTRODUCTION

Si-Ge heteroepitaxy has attracted much attention as a key technology for introducing the concept of band engineering into Si large-scale integrated circuits (LSIs).¹⁻³ Various studies have been reported about the fabrication of $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructure devices, for example, modulation-doped field-effect transistors (MODFETs),⁴⁻⁶ and heterojunction bipolar transistors (HBTs).⁷⁻⁹

For these applications, the density of defects such as misfit dislocations should be very low. It is known that a high-quality $\text{Si}_{1-x}\text{Ge}_x$ layer without any misfit dislocations can be grown on a Si substrate when the $\text{Si}_{1-x}\text{Ge}_x$ layer is thinner than a critical thickness which depends on the growth temperature and Ge composition x . However, post-thermal annealing at a temperature higher than the growth temperature introduces dislocations into these films, since the strained layer is not thermally stable. The introduction of dislocations degrades the device performance. This explains why the equilibrium critical thickness is smaller than the critical thickness.¹⁰

Therefore, to apply these structures to devices, it is necessary to suppress the generation of dislocations during thermal processes.^{11,12} To solve this problem, we investigated limited-area molecular-beam epitaxial (MBE) growth, in which a strained $\text{Si}_{1-x}\text{Ge}_x$ film was grown on a small Si region surrounded by SiO_2 (square SiO_2 openings). The results show that the dislocation density decreases as the area of the SiO_2 opening decreases.

This paper quantitatively studies the reduction in misfit dislocations achieved by limited-area MBE growth. In addition, it discusses the reduction mechanism from the point of view of the residual strain in the $\text{Si}_{1-x}\text{Ge}_x$ film.

II. EXPERIMENTS

First, a thermal oxide layer about 80 nm thick was formed on a Si (100) substrate. Square-shaped seed openings were then formed on the SiO_2 layer by conventional lithography and wet etching. These SiO_2 openings were oriented along the $\langle 110 \rangle$ direction ([011] and $[0\bar{1}\bar{1}]$) and the size of the SiO_2 openings was varied from 1×1 to

$100 \times 100 \mu\text{m}^2$. The substrates had both patterned and unpatterned regions for comparison.

The $\text{Si}_{1-x}\text{Ge}_x$ layers were grown using Vacuum Generator 366 MBE equipment. The base pressure of the growth chamber was below 1×10^{-8} Pa. Si and Ge were evaporated with an e-gun evaporator and a Knudsen cell, respectively. Both beam fluxes were monitored by quartz thickness monitors to control the alloy ratio x . The substrate temperature was measured using an optical pyrometer at high temperatures and a thermocouple at low temperatures. Before introducing the substrate into the growth chamber, the substrate surface was precleaned by chemical treatment, and a protective thin oxide layer was formed.¹³ Next, the thin oxide layer was sublimated at 850 °C for 20 min in the growth chamber to obtain a clean Si surface. After the substrate temperature was lowered to 520 °C, Si and Ge were coevaporated with a growth rate of 0.1–0.2 nm/s. The alloy ratios x were varied from 0.1 to 0.5 and the thicknesses of the $\text{Si}_{1-x}\text{Ge}_x$ films were 50 to 300 nm. The sample growth conditions are listed in Table I.

The crystal quality of the $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructure was investigated using a Hitachi H-700H transmission electron microscope (TEM) with an acceleration voltage of 200 kV. Plan-view TEM samples were prepared by chemical etching, and cross-sectional samples were made by mechanical thinning and Ar-ion sputtering. The residual strain in the $\text{Si}_{1-x}\text{Ge}_x$ film was measured by Raman scattering spectroscopy with a focused Ar-ion laser probe.

III. RESULTS AND DISCUSSION

Figure 1 shows a plan-view TEM image of the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si substrate without patterned SiO_2 . This TEM image includes the $\text{Si}_{0.8}\text{Ge}_{0.2}/\text{Si}$ heterointerface. Dislocations in the growth sample are mainly misfit dislocations extended along both $\langle 110 \rangle$ directions ([011] and $[0\bar{1}\bar{1}]$). The $\langle 110 \rangle$ directions are the cross line between the $\{100\}$ heterointerface and the $\{111\}$ glide plane of dislocations in the Si crystal; the misfit dislocations on the heterointerface must extend along the $\langle 110 \rangle$ directions. However, some of them do not lie along the $\langle 110 \rangle$ directions. The reason for this is not

TABLE I. List of samples. The alloy ratio x is the Ge fraction in the Si-Ge alloy.

Sample	Alloy ratio	Thickness (nm)
A	0.10	150
B	0.12	150
C	0.20	150
D	0.30	150
E	0.30	75
F	0.30	300
G	0.50	150

clear. The structure of misfit dislocations is studied now. A few threading dislocations connecting the misfit segments to the free surface were also observed. The linear dislocation density, which is defined as the reciprocal of the misfit dislocations spacing, is about $10\,000\text{ cm}^{-1}$. This value was averaged over both $\langle 110 \rangle$ directions. The linear dislocation density is much lower than the value estimated from the lattice mismatch (0.8%) between the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film and the Si substrate.

Typical TEM images of $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on a Si substrate with patterned SiO_2 are shown in Fig. 2. In these cases, single-crystal $\text{Si}_{0.8}\text{Ge}_{0.2}$ films grew on exposed Si regions (SiO_2 openings), and polycrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ grew on SiO_2 layers as shown in Fig. 3. Misfit dislocations occurred in the growth film along both $\langle 110 \rangle$ directions. These dislocations terminated at the boundaries between the single and polycrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ layers. The linear dislocation densities in $9.0 \times 9.0\text{ }\mu\text{m}^2$ [Fig. 2(a)], $7.0 \times 7.0\text{ }\mu\text{m}^2$ [Fig. 2(b)], and $4.5 \times 4.5\text{ }\mu\text{m}^2$ [Fig. 2(c)] squares were about 8000, 7000, and 5000 cm^{-1} . These linear dislocation densities are lower than those grown on a Si substrate without patterned SiO_2 . Dislocation-free $\text{Si}_{0.8}\text{Ge}_{0.2}$ layers could be formed on squares smaller than $2.5 \times 2.5\text{ }\mu\text{m}^2$ [Fig. 2(d)]. The relationship between these linear misfit dislocation densities and the square sizes is summarized in Fig. 4 for a 150-nm-thick $\text{Si}_{0.8}\text{Ge}_{0.2}$ film and a 75-nm-thick $\text{Si}_{0.7}\text{Ge}_{0.3}$ film. The linear dislocation densities were estimated by averaging TEM observations (for example,

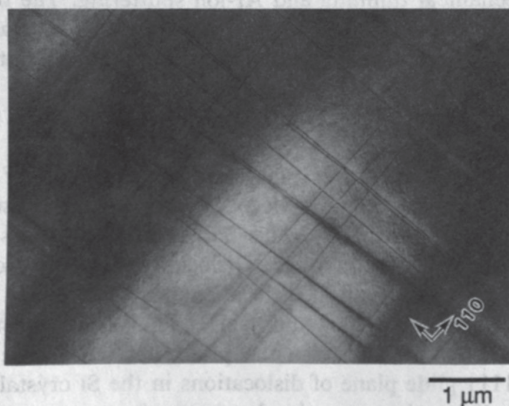
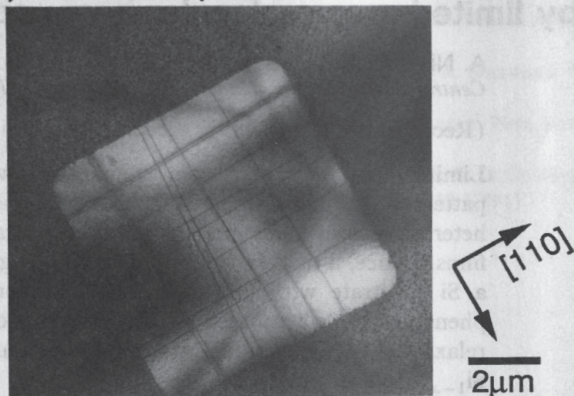
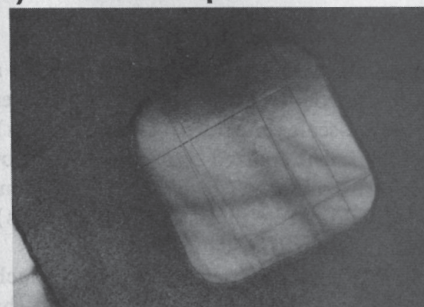


FIG. 1. A plan-view TEM image of $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si (100) substrate.

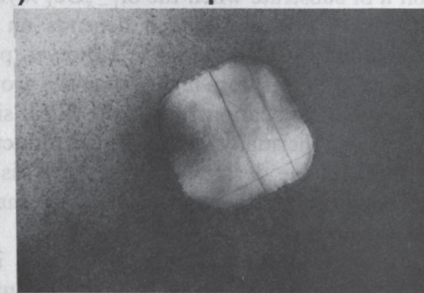
(a) $9.0 \times 9.0\text{ }\mu\text{m}^2$



(b) $7.0 \times 7.0\text{ }\mu\text{m}^2$



(c) $4.5 \times 4.5\text{ }\mu\text{m}^2$



(d) $2.5 \times 2.5\text{ }\mu\text{m}^2$

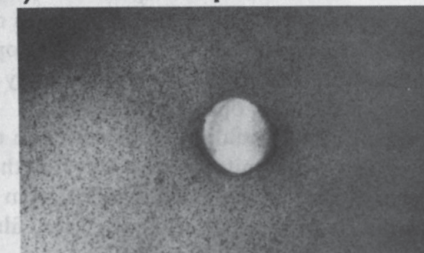


FIG. 2. Plan-view TEM images of $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si substrate with patterned SiO_2 of (a) 9.0×9.0 , (b) 7.0×7.0 , (c) 4.5×4.5 , and (d) $2.5 \times 2.5\text{ }\mu\text{m}^2$.

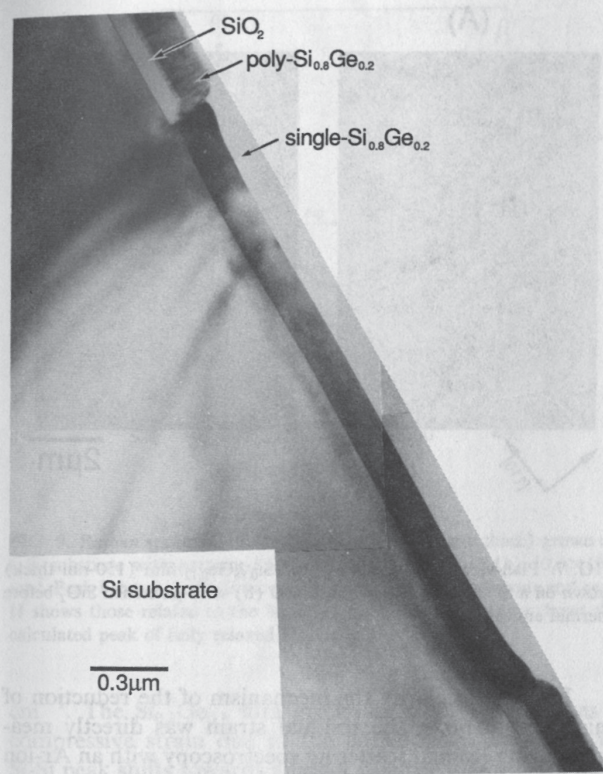


FIG. 3. A cross-sectional TEM image of $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si substrate with patterned SiO_2 .

the density for the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film on patterned $4 \times 4 \mu\text{m}^2$ SiO_2 was the average obtained from more than 130 areas). Figure 4 shows that this relationship can be divided into two regions (I and II). As the square SiO_2 opening length was decreased below $7 \mu\text{m}$ (region I), the linear dislocation density was rapidly reduced and had a linear dependence on the SiO_2 opening size. When the opening was larger than $7 \mu\text{m}$ (region II), the density was nearly independent of the size and had almost the same value as a film grown on a Si substrate without patterned SiO_2 .

There have been many studies on the critical thicknesses of $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ heterostructures. Figure 5 shows the critical thicknesses of $\text{Si}_{1-x}\text{Ge}_x$ films on Si substrates as a function of the Ge fraction. Results obtained by Kohama, Fukuda, and Seki using both the electron-beam-induced-current (EBIC) technique and TEM observations,¹⁴ are also shown in this figure. Our experimental critical thicknesses were determined by plan-view TEM observations. When $\text{Si}_{1-x}\text{Ge}_x$ films were grown on a Si substrate without a SiO_2 pattern, the only film without misfit dislocations was the 150-nm-thick $\text{Si}_{0.9}\text{Ge}_{0.1}$ film (sample A) (commensurate growth), and the others all had misfit dislocations (incommensurate growth). These results agree well with Kohama and co-workers' data. On the other hand, when the $\text{Si}_{1-x}\text{Ge}_x$ film was grown on a Si substrate with $2 \times 2 \mu\text{m}^2$ patterned SiO_2 , samples B, C, and D, as well as sample A, grew commensurately. For samples with $x=0.3$, the critical thicknesses of the films grown on patterned

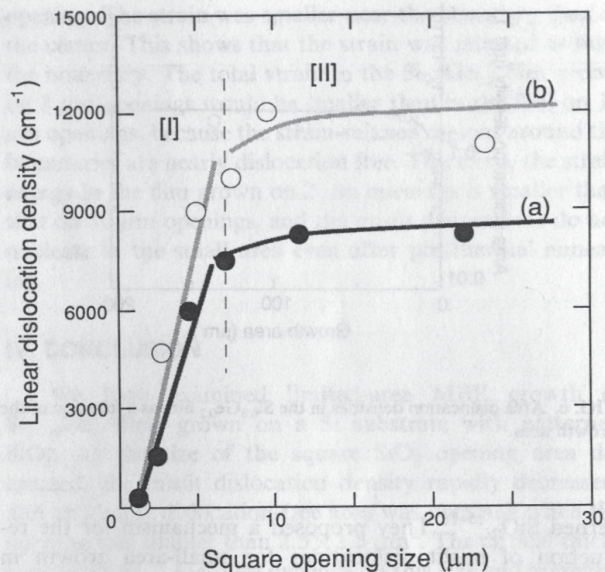


FIG. 4. Linear dislocation densities in $\text{Si}_{1-x}\text{Ge}_x$ film as a function of the size of the square SiO_2 opening. Line (a) shows results for the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) and line (b) shows results for the $\text{Si}_{0.7}\text{Ge}_{0.3}$ film (75 nm thick). These densities are the average values for misfit dislocations extending along both $[011]$ and $[0\bar{1}\bar{1}]$ directions.

SiO_2 were about three times larger than for those grown without patterned SiO_2 .

Recently, Fitzgerald *et al.*¹⁵ and Noble *et al.*¹⁶ have observed a significant reduction in misfit dislocation density on Si mesa structures and on Si substrates with pat-

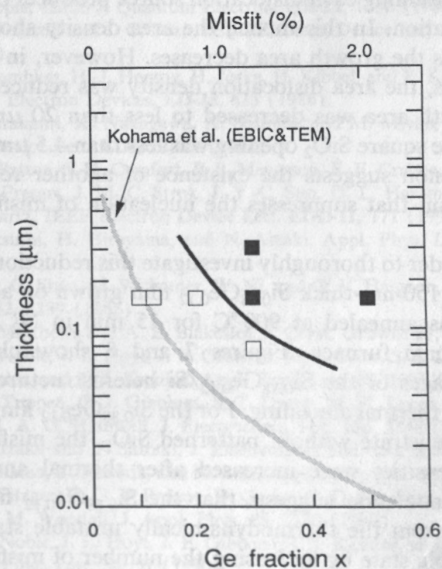


FIG. 5. Critical thicknesses of $\text{Si}_{1-x}\text{Ge}_x$ films on Si substrates with patterned SiO_2 of $2.0 \times 2.0 \mu\text{m}^2$, plotted as a function of Ge fraction x . The open and closed squares show the samples grown with and without misfit dislocations, respectively. The results by Kohama and co-workers (Ref. 14) (without patterned SiO_2) are also shown.

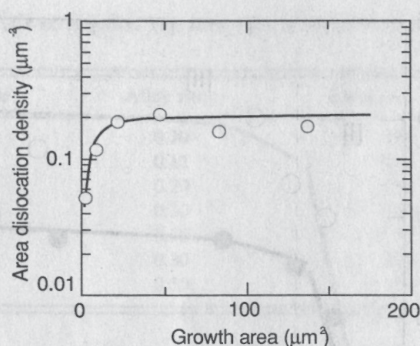


FIG. 6. Area dislocation densities in the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film as a function of the growth area.

terned SiO_2 .¹⁵⁻¹⁸ They proposed a mechanism for the reduction of misfit dislocations for small-area growth in lattice-mismatched systems. The proposed mechanism says that the extension of misfit dislocations is limited by the trench layer of the mesa structure or by the polycrystalline layer on patterned SiO_2 . In other words, a misfit dislocation that nucleates on one area, which is surrounded by a trench or polycrystalline layer, cannot extend to another area as it is blocked by the trench or polycrystalline region. Our experiments also showed the linear dependence of the dislocation density on the SiO_2 opening size in region I (Fig. 4); this agrees with the model of Fitzgerald *et al.* Figure 6 shows data replotted from region I of Fig. 4. The horizontal axis shows the area of the square SiO_2 opening and the vertical axis shows the area density of misfit dislocations. This area dislocation density corresponds to the density of the dislocation sources in the above-mentioned model, assuming each dislocation source produces one misfit dislocation. In this model, the area density should not change as the growth area decreases. However, in our experiments, the area dislocation density was reduced when the growth area was decreased to less than $20 \mu\text{m}^2$ (the size of the square SiO_2 opening was less than $4.5 \mu\text{m}$). This phenomenon suggests the existence of another reduction mechanism that suppresses the nucleation of misfit dislocations.

In order to thoroughly investigate this reduction mechanism, a 150-nm-thick $\text{Si}_{0.88}\text{Ge}_{0.12}$ film grown on a Si substrate was annealed at 900°C for 15 min in N_2 using a conventional furnace. Figures 7 and 8 show plan-view TEM images of the $\text{Si}_{0.88}\text{Ge}_{0.12}$ /Si heterostructure before and after thermal annealing. For the $\text{Si}_{0.88}\text{Ge}_{0.12}$ film grown on a Si substrate without patterned SiO_2 , the misfit dislocation densities were increased after thermal annealing. This phenomenon suggests that the $\text{Si}_{0.88}\text{Ge}_{0.12}$ film was changed from the thermodynamically unstable state to a more stable state by increasing the number of misfit dislocations. For the $\text{Si}_{0.88}\text{Ge}_{0.12}$ film grown on a Si substrate with patterned SiO_2 , the misfit dislocation density was not changed after thermal annealing. This is presumably because the strain in the as-grown film was partially relaxed and was stable enough without misfit dislocations.

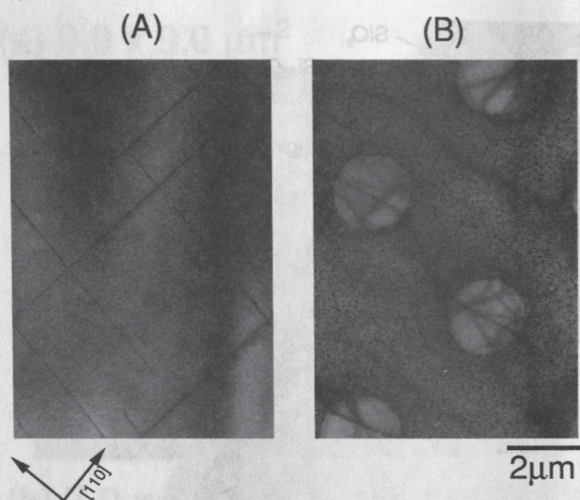


FIG. 7. Plan-view TEM images of the $\text{Si}_{0.88}\text{Ge}_{0.12}$ film (150 nm thick) grown on a Si substrate (a) without and (b) with patterned SiO_2 before thermal annealing.

In order to clarify the mechanism of the reduction of misfit dislocations, the residual strain was directly measured using Raman scattering spectroscopy with an Ar-ion laser. The beam diameter was about $1 \mu\text{m}$. Figure 9 shows typical Raman spectra from the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si substrate with 2 and $10 \mu\text{m}$ patterned SiO_2 . Two peaks were observed, at about 520 and 515 cm^{-1} , on both spectra in Fig. 9. The stronger peak at 520 cm^{-1} was related to Si-Si vibrations from the Si substrate and the weak peak at 515 cm^{-1} was from the strained $\text{Si}_{0.8}\text{Ge}_{0.2}$ film on the Si substrate. In accordance with the previous results,¹⁹ a peak related to Si-Si vibrations from the bulk $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloy was calculated to be at about 507.8

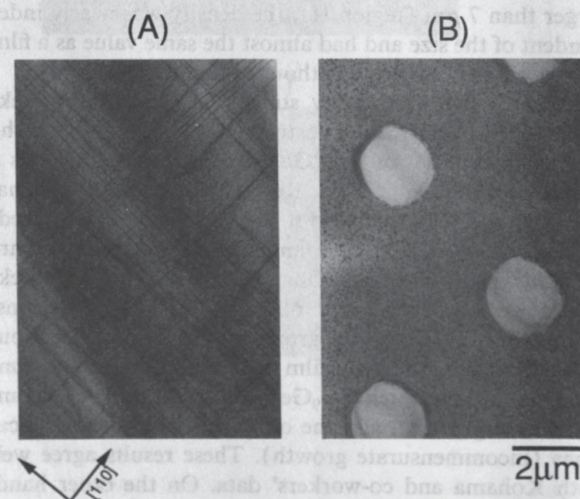


FIG. 8. Plan-view TEM images of the $\text{Si}_{0.88}\text{Ge}_{0.12}$ film (150 nm thick) grown on a Si substrate (a) without and (b) with patterned SiO_2 after thermal annealing.

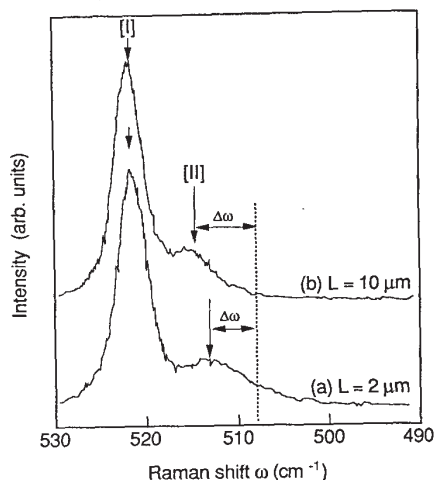


FIG. 9. Raman spectrum of the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film (150 nm thick) grown on a Si substrate with patterned SiO_2 of (a) 2.5×2.5 and (b) 10.0×10.0 μm^2 . Peak I shows the Si-Si vibrations related to the Si substrate and peak II shows those related to the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film. The broken line shows the calculated peak of fully relaxed $\text{Si}_{0.8}\text{Ge}_{0.2}$.

cm^{-1} . The $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on a Si substrate has a compressive strain due to the lattice mismatch, and the Si-Si peak shifts towards a larger number than that of bulk $\text{Si}_{0.8}\text{Ge}_{0.2}$. The residual strain can be estimated using the following relationship:

$$\Delta\omega = b\epsilon \quad (\text{cm}^{-1}).$$

Here $\Delta\omega$ is the frequency difference between the measured peak and the bulk peaks, and b is an experimental fitting parameter, calculated as $b = 24$ (cm^{-1}) from the relationship between the Raman shift and lattice mismatch.²⁰ The estimated residual strain was 1.03% for the 150-nm-thick $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on 10 μm SiO_2 openings, and 0.61% for the film grown on 2 μm openings. To study the mechanism of strain reduction, we measured the distribution of the residual strain in the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on 10 μm SiO_2 openings. Figure 10 shows the strain as a function of the distance from the boundary between the crystal and the polycrystalline $\text{Si}_{0.8}\text{Ge}_{0.2}$ film to the center of the SiO_2

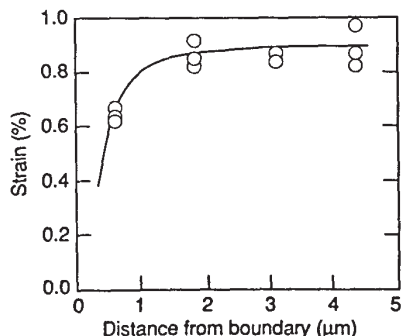


FIG. 10. Residual strain distribution in the 150-nm-thick $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on a Si substrate with patterned SiO_2 of 10.0×10.0 μm^2 .

opening. The strain was smaller near the boundary than in the center. This shows that the strain was released around the boundary. The total strain in the $\text{Si}_{0.8}\text{Ge}_{0.2}$ film grown on 2 μm openings would be smaller than in the film on 10 μm openings, because the strain-relaxed regions around the boundaries are nearly dislocation free. Therefore, the strain energy in the film grown on 2 μm openings is smaller than that on 10 μm openings, and the misfit dislocations do not nucleate in the small area even after postthermal annealing.

IV. CONCLUSION

We have examined limited-area MBE growth of $\text{Si}_{1-x}\text{Ge}_x$ films grown on a Si substrate with patterned SiO_2 . As the size of the square SiO_2 opening area decreased, the misfit dislocation density rapidly decreased, and an almost dislocation-free area was obtained when the opening was smaller than 2.5×2.5 μm^2 . The critical thickness of the $\text{Si}_{1-x}\text{Ge}_x$ film depends on this size and increases as the size is reduced. The reduction in misfit dislocations can be attributed not only to the blocking of the misfit dislocation extension but also to the relaxation of the residual strain in the boundary between single-crystal and polycrystalline $\text{Si}_{1-x}\text{Ge}_x$ film.

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