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Thermal Relaxation of Strained SiGe/Si Heterostructure

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The lattice strain of SiGe/Si relaxes upon annealing, but the relaxation speed decreases with time according to the change in the residual strain. This menchanism is expected to produce the metastability which has been observed in SiGe/Si strained structures. The deceleration process was interpreted comprehensively by the dislocation glide dynamics based on the thermal activation process, where the activation energy E depends linearly on the applied shear stress σ as high as ~ 1 GPa. The stress dependence of the activation energy $\Delta E/\Delta\sigma$ obtained experimentally was $\sim 2\times10^{-28}$ m^3.

KEYWORDS: molecular beam epitaxy, silicon germanium, heteroepitaxy, critical thickness, misfit dislocation, metastability, thermal relaxation

§1. Introduction

Recently, the strained-layer epitaxy of semiconductors has received considerable attention. The built-in strain has dramatic effects on the band structure of the materials, which therefore have potential applications to a variety of interesting semiconductor devices. However, the thickness of such a strained layer is limited to a critical value h_c, above which plastic relaxation occurs by formation of misfit dislocations. The following discrepancies have been observed between experimental results and theories: (1) the critical thicknesses obtained experimentally are several times larger than the values predicted by theories and (2) the sample temperature has considerable influence on the value of the critical thickness (metastability). Several models have been proposed to explain the large critical thickness; however, the mechanism of metastability has not been clarified.[1-9]

In the schema of the theories assuming energy balance and mechanical balance,[1-9] the equations do not explicitly include the temperature dependence. Therefore, when the sample temperature is increased from T to $T+\Delta T$, the balance point shifts by the change in the elastic energy of the epitaxial layer due to the thermal expansion of the sample, and the thermal relaxation occurs to compensate for it.[6] Since the value of $\Delta h/h$ (h: epitaxial layer thickness) can be neglected compared to the value of $\Delta\varepsilon_r/\varepsilon_r$, the increase of the strain $\Delta\varepsilon_r$ due to annealing will be relaxed almost completely by the formation of the misfit dislocations: $\varepsilon_r(T)=\varepsilon_r(T+\Delta T)$. This prediction does not agree with the experimental results which have been observed.

Dodson and Tsao recently introduced the thermal activation process based on the dislocation dynamics to explain the experimental results written above.[10] They compared their model with the experimental results regarding the critical thickness and they showed the dislocation glide activation energy to be stress dependent.

In this letter, we show the stress dependence of the dislocation glide activation energy and the mechanism of the metastability directly by analyzing the thermal relaxation of the lattice strain upon annealing.

§2. Scheme for the Analysis

When the thermal relaxation of the lattice strain is limited by the thermally activated dislocation glide process, the relaxation velocity can be written by

$$\mathrm{d}\delta/\mathrm{d}t \propto \rho\cdot\sigma^m\cdot\exp\left(-E(\sigma)/kT\right) \tag{1}$$

$$E(\sigma)=E(0)-D\cdot\sigma \tag{2}$$

where $E(\sigma)$ is the stress dependent activation energy for the dislocation glide, ρ is the dislocation density in the epitaxial layer, σ is the effective stress exerted on a dislocation, which corresponds to the "excess stress" in Tsao *et al.*'s model,[7] $m\sim1$ and the structure of the coefficient D depends on the microscopic mechanism.

When the exponential factors in eq. (1), upon annealing at T and $T+\Delta T$ are equal each other, eq. (1) gives the relationship between ΔE and ΔT as

$$\Delta E=(E/T)\cdot\Delta T. \tag{3}$$

If the stress and the temperature dependence of D is small, ideally zero, eq. (2) gives the relation of $\Delta E=D\cdot\Delta\sigma$. Substituting the relation into eq. (3), the activation energy at T can be given by

$$E=D\cdot(\Delta\sigma/\Delta T)\cdot T. \tag{4}$$

Combining eqs. (2) and (4), the coefficient D can be written by

$$D=E(0)\cdot(\sigma+(\Delta\sigma/\Delta T)\cdot T)^{-1}. \tag{5}$$

Therefore, by measuring the residual strains which give the same exponential factor, approximately close dislocation velocities, upon annealing at T and $T+\Delta T$, the values of D and $E(\sigma)$ can be obtained experimentally.

Under the mechanism written above, the activation energy increases with the decrease of the lattice strain by annealing, and if the relaxation speed becomes low enough compared to the observation time scale, the apparent stability (metastable state) will appear.

§3. Experimental and Results

Epitaxial SiGe layers were grown on Si(001)2×1 substrates with a combination of an electron-beam evaporator for Si and a Knudsen cell for Ge, where the substrate temperature was kept at 550°C. The pressure was basically 2×10^{-10} Torr and was kept below 3×10^{-9} Torr during the crystal growth. The deposition rate of Si was fixed (0.15 nm/s) and Ge fractions were controlled by adjusting the temperature of the Knudsen cell. Samples were annealed in Ar atmosphere, and the amount of the thermal relaxation of the strained SiGe layer upon each annealing was obtained by X-ray diffraction at room temperature through the measurement of the (400) peak shift.

Figure 1 shows the typical result about the thermal relaxations of $Si_{1-x}Ge_x$ strained lattices ($x=0.2$, $h=400$ nm and $h=250$ nm). Samples were annealed in two different ways: (1) three steps, 650°C→750°C→850°C (solid lines in Fig. 1) and (2) 850°C from the beginning (dashed lines in Fig. 1). The values of the lattice constants decrease with time; however, the relaxation velocities are lowered and become almost stable at each annealing temperature within the experimental time scale (~1 hour).

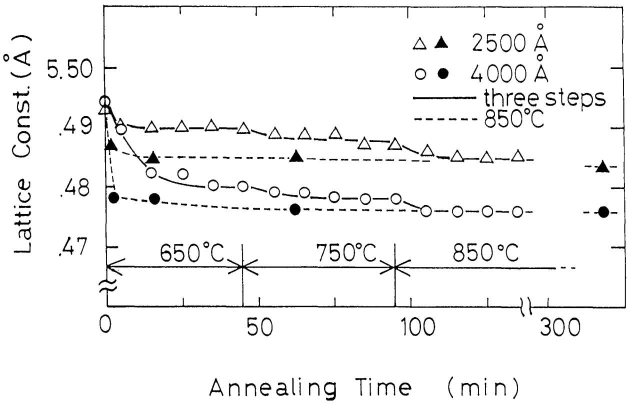

Fig. 1. Thermal relaxation of the $Si_{1-x}Ge_x$/Si strained heterostructure($x=0.2$, $h=250$ and 400 nm) through two different annealing procedures: 1) three steps, 650°C→750°C→850°C (solid lines), 2) 850°C from the beginning (dashed lines).

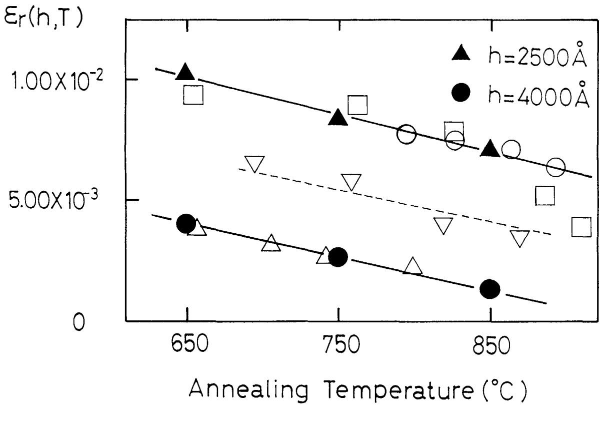

Fig. 2. Residual strains in epitaxial layers of $Si_{1-x}Ge_x$/Si ($x=0.2$, $h=250$, 400 nm) at the plateaus of $T=650$, 750 and 850°C in Fig. 1. Data obtained by Hull and Been were calibrated and are drawn together (△: $X=0.15$, $h=300$ nm, □: $x=0.25$, $h=35$ nm, ▽: $x=0.17$, $h=100$ nm, capped by 300 nm Si layer, ○: $x=0.2$, $h=100$ nm, capped by 300 nm Si layer).[11,12]

Figure 2 shows the relation between the residual strains at the plateaus shown in Fig. 1 and the annealing temperature. The strains ε_r were calculated from the values of measured ($d_r(T)$) and strain-free ($d_x(T)$) lattice constants of $Si_{1-x}Ge_x$ at T by

$$\varepsilon_r=(d_r(T)-d_x(T))/(d_x(T)\cdot\gamma) \tag{6}$$

(γ: Poisson's ratio, h: epitaxial layer thickness). The effect of the thermal expansion is included.

The temperature dependence of the residual strain is linear. When the absolute values of the residual strain are calculated from the experimental values, they are very sensitive to the value of the Ge ratio in the SiGe layer; however, the Ge ratio dependence of the gradients in Fig. 2 was negligible.

§4. Discussion

The linear relationship of $\Delta\sigma\propto\Delta T$ shown in Fig. 2 indicates the dislocation velocities (the exponential factor in eq. (1) to be accurate) at the plateaus in Fig. 1 to be close enough each other to use eqs. (4) and (5). Substituting the values of $E(0)=2.0$ eV (obtained by the interpolation of the equivalent activation energies for the bulk Ge, 1.6 eV and for the bulk Si, 2.2 eV), $\Delta T=100$°C, $T=650$°C, $\Delta\sigma\sim1.2\times10^8$ Pa, and $\sigma\sim3\times10^8$ Pa into eq. (5); the value of D becomes $\sim2\times10^{-28}$ m^3. This value agrees well with the value expected according to the usual dislocation dynamics models.

The value of $E(\sigma)$ at the plateau of $T=650$°C can be determined by eq. (4) as ~1.5 eV ($E/kT\sim20$). The value of the activation energy obtained here is markedly higher than the value of 1.1 eV obtained by Hull and Bean.[11] The difference comes from the lowering of the excess stress in eq. (2) by the strain relaxation upon annealing. Such mechanism decelerates the relaxation speed as is mentioned in §2 and gives the plateaus observed in Fig. 1.

Since the maximum shear stress in our experiment is ~1 GPa, the linear stress dependence of the activation energy on the applied shear stress is maintained as high as ~1 GPa.

In addition, Hull and Bean[11,12] and Hull *et al.*[13] observed the change in the misfit dislocation density for the SiGe/Si and Si/SiGe/Si structures upon successive 5 minute annealings at the relevant temperature using the in situ electron microscope. We calibrated their experimental values roughly by assuming 100% dependence of the strain relaxation on the dislocation density, and the results are drawn together in Fig. 2 (△: $x=0.15$, $h=300$ nm, □: $x=0.25$, $h=35$ nm, ▽: $x=0.17$, $h=100$ nm, capped by 300 nm Si layer, ○: $x=0.2$, $h=100$ nm, capped by 300 nm Si layer). Five minutes may not be sufficient to equalize the dislocation velocity at each temperature, but some of them show the linear relation of $\Delta\varepsilon\propto\Delta T$ and the gradients of $\Delta\varepsilon/\Delta T$ for the both structures seem to be almost equal each other in Fig. 2. Including the analysis of the h-dependence, more detailed experiments must be performed to discuss the mechanism further.

Since the activation energy must be reduced by the strain according to eq. (2), additional mechanisms are necessary to interpret the high activation energy of 2.2 eV obtained by Hull and Bean for the double heterostructure in the early stage of relaxation.[11)]

§4. Conclusion

The thermal relaxation of the strained SiGe/Si heterostructure was found to be governed by the built-in strain in the epitaxial layer and the annealing temperature, and was interpreted by the dislocation glide dynamics based on the thermal activation process, where the activation energy E depends linearly on the applied shear stress σ as high as ~ 1 GPa.

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Note added in proof—Very recently, a related paper was published by Hull *et al.*,[14)] where they analyzed their data (□ in Fig. 2) using Dodson and Tsao's model with the assumption of the dislocation interaction.[10)] They obtained the value of $1.9 \sim 2.9 \times 10^{-28}$ m^3 for the coefficient D in eq. (2) by observing the dislocation dynamics during the early stages of the strain relaxation process, and they used the value of 2.1×10^{-28} m^3 to make a good fitting, the value of which is in good agreement with our result.

The temperature which gives the same ratio of $E/kT(\sim 20)$ for $E=1.1$ eV is about 400°C, which can be compared with the low dislocation velocity at 400°C observed by them.