Strain modification in coherent Ge and Si_xGe_{1-x} epitaxial films by ion-assisted molecular beam epitaxy

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We have observed large changes in Ge and Si_xGe_{1-x} layer strain during concurrent molecular beam epitaxial growth and low-energy bombardment. Layers are uniformly strained, coherent with the substrate, and contain no dislocations, suggesting that misfit strain is accommodated by free volume changes associated with injection of ion bombardment induced point defects. The dependence of layer strain on ion energy, ion-atom flux ratio, and temperature is consistent with the presence of a uniform dispersion of point defects at high concentration. Implications for distinguishing ion-surface interactions from ion-bulk interactions are discussed.

Low-energy ion bombardment has been employed in several contexts in epitaxial growth, most commonly as a method for surface cleaning prior to growth. More recently, ion bombardment has been employed during growth for enhanced dopant incorporation[1] in Si, and surface cleaning during growth as in plasma-enhanced chemical vapor deposition of Si.[2] Direct low-energy ion beam deposition has produced epitaxial films of Si, Ge, and GaAs,[3] and notably has yielded epitaxial Si films at temperatures as low as 100 °C.[4]

Improved understanding of ion-surface interactions during growth may yield additional elements of control over epitaxial film structure, strain state, and composition. Of particular interest for high quality epitaxial films is the identification of the regime in which surface and near-surface processes, such as surface diffusion and incorporation at growth sites, can be enhanced at low temperatures while avoiding or controlling damage in the deposited films. Recent *in situ* studies of molecular beam epitaxial growth of Ge demonstrated that the surface morphology during steady-state growth[5,6] or ion bombardment[7] results from a kinetic competition between surface defect creation and surface defect annihilation.

There is also considerable interest in the development of techniques for control of strain in thin films and application of such techniques to strained-layer heteroepitaxy. Here we report controlled modification of perpendicular strain by up to 1.5% in coherent Ge and Si_xGe_{1-x} films grown on (001)Ge substrates by defect injection during ion-assisted molecular beam epitaxy (IAMBE), and discuss the implications for understanding ion-surface interactions.

Films were grown in a custom-designed molecular beam epitaxy system with a base pressure of 1×10^{-10} Torr, which was equipped with electron beam sources for deposition of Si and Ge. Strain-modified films 100 nm were grown at constant rate in the range 0.1–0.7 nm/s on (001) Ge substrates, following growth of a 50 nm buffer layer of pure Ge by conventional molecular beam epitaxy. Concurrent ion bombardment was accomplished using a Kaufmann-type ion source capable of Ar^+ ion bombardment during growth at energies of 50–1500 eV. Ion beam current density was measured using both a Faraday cup mounted adjacent to the Mo substrate block and measurement of ion current at the substrate block, and ion-atom flux ratios were typically in the range 1:10–1:100. Growth temperatures were in the range of 200–450 °C. Films were analyzed *in situ* using reflection high-energy electron diffraction (RHEED), and following growth by double-crystal x-ray diffractometry using Fe K_α radiation. Some samples were also analyzed using a four-crystal high-resolution x-ray diffractometer[8] using Cu K_α radiation, and by cross-sectional transmission electron microscopy.

The strain state for a 100-nm-thick Ge film on (001) Ge grown by IAMBE is illustrated by the x-ray rocking curves in Fig. 1(a), taken around the (004). The film was grown on top of a 50 nm Ge buffer layer grown by conventional MBE at $T = 300$ °C, at a growth rate of 0.3 nm/s with an ion energy of $E_i = 200$ eV and ion/atom flux ratio of $J_i/J_a = 0.03$. In the rocking curve scan around (004) diffraction plane, a sharp Bragg peak of instrumentation-limited width is observed at angular shift of $\Delta\theta = -0.44°$ from the substrate Bragg peak. The parallel strain was further examined by taking diffraction around (224) plane of the sample using high-resolution x-ray diffractometry.[8] Dynamical theory of x-ray diffraction[9] was used to simulate the experimental data. The results indicate the presence of a coherent film with perpendicular strain resulting in a tetragonal distortion such that $\epsilon_\perp = 0.82\%$. The post-growth RHEED pattern taken at 20 keV along a [110] azimuth provides a qualitative indication of a smooth surface morphology. The (2×1) reconstruction characteristic of a clean (001) Ge surface is also observed. Cross-sectional transmission electron microscopy indicated the 100 nm film to be free of misfit dislocations, threading dislocations, and stacking faults indicating that strain modification did not occur as a result of introduction of linear or planar defects.

Figure 1(b) shows similar results for a $Si_{0.2}Ge_{0.8}$ layer grown on Ge (001) by IAMBE at a growth rate of 0.25 nm/s with an ion energy of $E_i = 200$ eV and ion/atom flux ratio of $J_i/J_a = 0.03$. In the rocking curve scan around (004) diffraction plane, the Bragg peak from the 250 nm film occurs at $\Delta\theta = 0.2°$ with respect to the substrate Bragg peak. It should be noted that a coherent film with this alloy composition grown by conventional MBE exhibits a Bragg

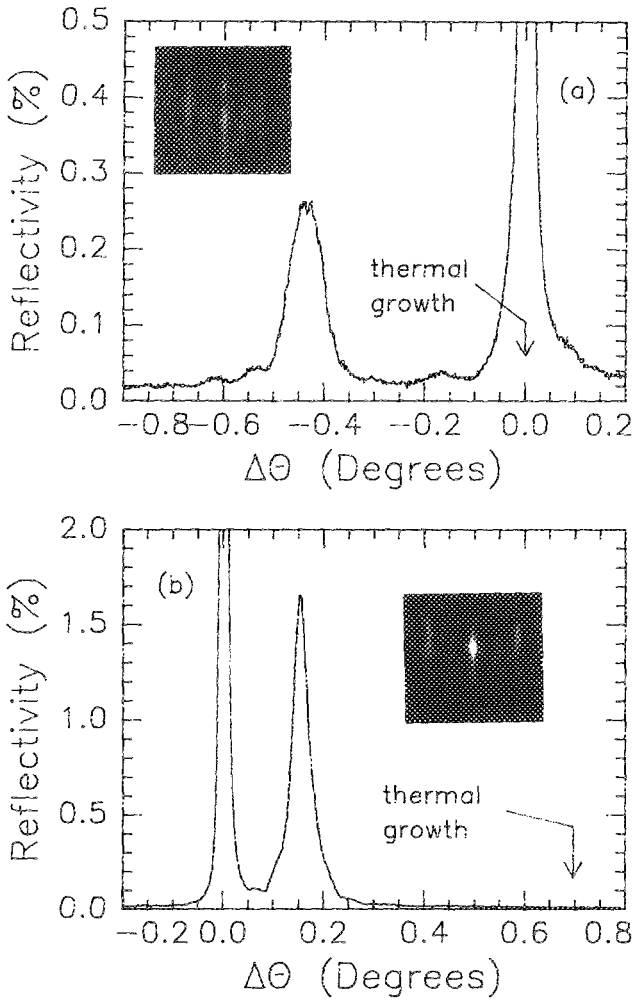

FIG. 1. (a) X-ray rocking curve around (004) Bragg peak for a 100 nm Ge film grown on (001) Ge by IAMBE at $T = 300\,^{\circ}C$ for an ion/atom flux ratio $J_i/J_a = 0.03$, and incident Ar^+ ion beam energy $E_i = 200$ eV. 20 keV RHEED pattern at incidence angle of 2° is shown as inset. (b) X-ray rocking curve around (004) Bragg peak for a 250 nm $Si_{0.2}Ge_{0.8}$/(001) Ge grown by IAMBE at $T = 300\,^{\circ}C$; ion/atom flux ratio $J_i/J_a = 0.03$; incident Ar^+ ion beam energy $E_i = 200$ eV. 20 keV RHEED pattern at incidence angle of 2° is shown as inset.

peak at $\Delta\theta = 0.7°$, with an associated strain of $\epsilon_\perp = -1.3\%$. The magnitude and sign of strain modification are nearly equal for the pure Ge film and $Si_{0.8}Ge_{0.2}$ alloy, strongly suggesting that the normally tensile strain in the $Si_{0.2}Ge_{0.8}$ alloy was compensated by point defects introduced by IAMBE growth.

The variation of perpendicular strain, $\epsilon_\perp$, with ion/atom flux ratio J_i/J_a, for 100-nm-thick Ge films grown on Ge(001) by IAMBE is shown in Fig. 2, for films grown at $T = 300\,^{\circ}C$ with an Ar ion energy of $E_i = 200$ eV. An approximately linear relationship exists between perpendicular strain $\epsilon_\perp$ and ion-atom flux ratio $J_i/J_a = 0$–0.05. For higher ion-atom flux ratios, no strain modification was observed. For ion-atom flux ratios above 0.06, the Bragg peak from the strain-modified film broadens and is reduced in intensity. For $J_i/J_a \geqslant 0.1$, the RHEED pattern is characterized by Bragg diffraction spots rather than rods, indicating qualitatively the development of a rough surface morphology.

The variation of perpendicular strain $\epsilon_\perp$ with incident

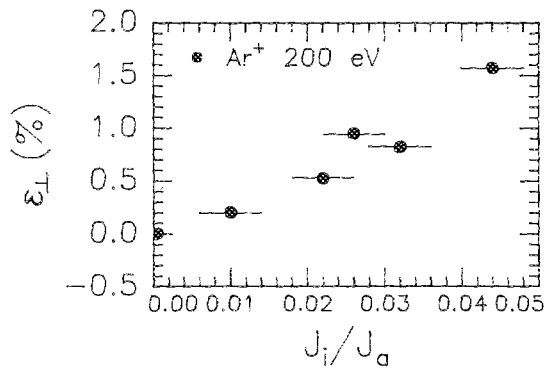

FIG. 2. Variation of perpendicular strain, $\epsilon_\perp$, with ion/atom flux ratio J_i/J_a at the surface for 100-nm-thick Ge films grown on Ge (001) by IAMBE at $T = 300\,^{\circ}C$. All films grown with Ar ion energy of $E_i = 200$ eV.

ion energy E_i for 100-nm-thick Ge films grown on Ge substrates by IAMBE at $T = 300\,^{\circ}C$ is illustrated in Fig. 3. The ion-atom flux ratio at the surface was fixed at $J_i/J_a = 0.02$. Strain increases monotonically with incident ion energy in the energy regime $E_i = 70$–300 eV. For ion energies below 70 eV under these growth conditions, no detectable strain modification is observed. We believe that the present measurements of coherent perpendicular strain as a function of energy represent possibly the most sensitive measurement to date of the ion energy regime for the transition from displacement of only surface atoms to the displacement of bulk atoms as well as surface atoms. Brice *et al.* have suggested a conceptual framework for partitioning of surface and bulk displacements at low ion energies.[10] Interestingly, their calculations suggest that the surface-to-bulk displacement ratio R varies from $R = 1.6$ at $E_i = 100$ eV to $R = 8$ at $E_i = 50$ eV for Ar^+ ions incident on Ge surfaces. While the close agreement between their estimation of this transitional energy regime for onset of bulk displacements in Ge and the transitional regime for strain modification in the present experiments may be fortuitous, our results suggest that measurement of strain modification by injection of point defects into the bulk may be a powerful tool for delineation of this regime.

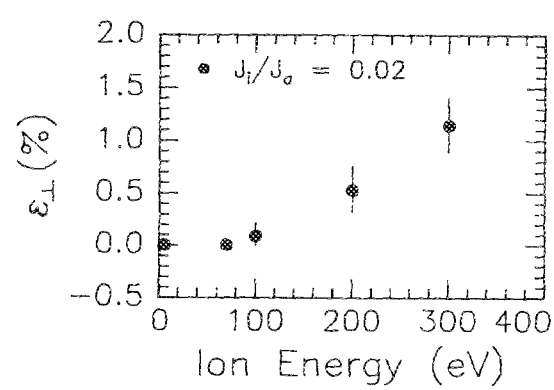

FIG. 3. Variation of perpendicular strain, $\epsilon_\perp$, with incident ion energy, E_i, for 100-nm-thick Ge films grown on Ge substrates by IAMBE at $T = 300\,^{\circ}C$. Ion-atom flux ratio at the surface was fixed at $J_i/J_a = 0.02$. Error bars indicate the uncertainty introduced by possible variations in the ion-atom ratio, J_i/J_a.

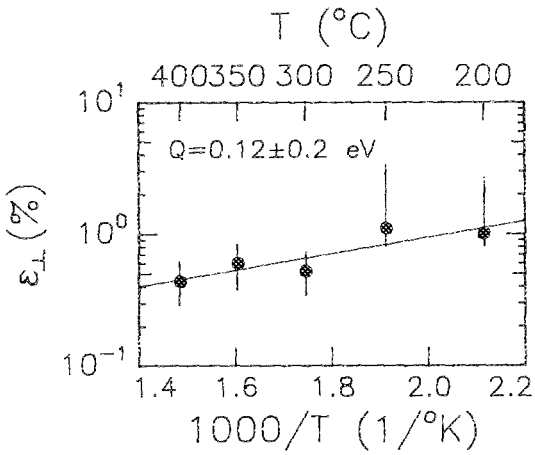

FIG. 4. Variation of perpendicular strain, $\epsilon_\perp$, with temperature for 100-nm-thick Ge films grown on Ge substrates by IAMBE. Ion-atom flux ratio at the surface was fixed at $J_i/J_a = 0.02$, and ion energy at $E_i = 200$ eV. Error bars indicate the uncertainty introduced by possible variations in the ion-atom flux ratio, J_i/J_a.

The variation of perpendicular strain $\epsilon_\perp$ with temperature for 100-nm-thick Ge films grown on Ge substrates by IAMBE is shown in Fig. 4. The ion-atom flux ratio at the surface was fixed at $J_i/J_a = 0.02$, and ion energy was fixed at $E_i = 200$ eV. The Arrhenius plot indicates an apparent activation energy of $Q_{sr} = 0.12 \pm 0.2$ eV for the dissociation of the rate-limiting process for strain reduction. It is not possible at present to specifically identify the defect associated with strain modification; however, a few observations are in order. The migration kinetics of simple interstitials in Ge are not well understood, but interstitial motion in Si is essentially athermal,[11] hence the observation of a nonzero activation energy for defect annihilation suggests that interstitial migration may not be the rate-limiting event. The activation energy Q_{sr} is lower than that estimated for vacancy migration in bulk Ge,[12] but is similar to the activation energy for grain boundary motion during high-energy ion irradiation induced grain growth in Ge.[13]

One possible interpretation of the kinetic process of strain modification is that (i) native point defects and inert gas atoms are injected into the near surface region; (ii) the predominant defect removal process is annihilation at the free surface, which represents a fixed sink for point defects, and that the sink strength is approximately independent of temperature; (iii) the apparent activation energy thus represents the temperature dependence of the mobility of an as yet unspecified point defect, or the temperature dependence for dissociation of a complex of point defects, in the near-surface region. Although we cannot demonstrate the uniqueness of this interpretation, the linear dependence of perpendicular strain on ion/atom flux ratio, i.e., $\epsilon_\perp \propto J_i/J_a$, supports the argument for defect annihilation at a fixed sink. If defect annihilation occurred in a bimolecular recombination process, such as vacancy-interstitial recombination, we would instead expect to observe $\epsilon_\perp \propto (J_i/J_a)^{1/2}$.[14]

To elucidate the relative roles of native point defects and trapped gas in strain modification, thermally stimulated gas evolution was correlated with strain relaxation. The rate of Ar evolution was measured as a function of temperature *in situ* immediately following growth for several samples by quadrupole mass spectrometry scans at a constant heating rate of 1 °C/s in the temperature range $T = 200$–500 °C. The onset of Ar evolution in pure Ge films occurred at approximately $T = 300$ °C, whereas the onset of strain relaxation occurred at $T = 500$–600 °C.

In another set of experiments, Rutherford backscattering spectrometry (RBS) was also used to measure trapped gas concentration directly in films grown by IAMBE. To enhance the sensitivity of the measurements of gas concentration by RBS, 200 eV Xe^+ ions were employed rather than Ar^+. Briefly, for films grown with an ion/atom flux ratio $J_i/J_a = 0.13$, which exhibited a strain of 0.61% ($\epsilon_\perp = 0.0061$), the concentration of Xe gas trapped in the film was found to be approximately 0.4%. From these observations it was not possible to determine whether the point defect or defect complex responsible for strain is a native point defect or a complex involving trapped noble gases. Additional experiments to resolve the question are under way.

In summary, we have observed changes in Ge and Si_xGe_{1-x} layer strain by up to 1.5% during concurrent molecular beam epitaxial growth and low-energy ion bombardment (IAMBE). The films are coherent and dislocation-free. The dependence of layer strain on ion energy, ion-atom flux ratio, and temperature is consistent with a model in which misfit strain is accommodated by free volume changes associated with injection of a uniform dispersion of point defects at high concentration. The variation of strain with Ar ion energy suggests that the ratio of surface displacements to bulk displacements is large for energies below $E_i = 70$ eV. The rate-limiting process in strain modification by IAMBE appears to be defect annihilation at the free surface during growth.

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