X-ray scattering studies of surfactant mediated epitaxial growth of Si/Ge/Si(001) heterostructures

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The strain and morphology of Si/Ge films grown by surfactant mediated molecular beam epitaxy on Si(001) with Bi as the surfactant were studied with grazing-incidence x-ray diffraction, x-ray reflectivity, low-energy electron diffraction, and Auger electron spectroscopy. Bi is observed to prevent the intermixing of Ge and Si layers by inhibiting Ge segregation in Si. Without a surfactant the critical thickness of Ge/Si(001) is 3 monolayers (ML). Using Bi, two-dimensional growth of Ge is observed for films up to 10 ML in thickness, with the onset of strain relaxation occurring at 7 ML of Ge growth. At 10 ML, the top Ge atomic layers are only partially relaxed. This is achieved by introducing roughness at the interface of the Ge and Si layers. © *2000 American Institute of Physics.* [S0021-8979(00)07418-1]

I. INTRODUCTION

The epitaxial growth of lattice mismatched heterostructures is a nonequilibrium process that is driven by surface kinetics and strain relaxation. Surfactants have been shown to modify the morphology of lattice mismatched heterolayers. Under metastable growth conditions, the surfactant causes a decrease in surface energy at the growth layer, which aids the wetting process of the epilayer.[1] The lattice mismatch between Si and Ge is 4.2% and the surface energy of Ge is lower than that of Si. Therefore, Ge growth on Si is in Stranski–Krastanov mode which is a two-dimensional layer by layer growth up to 3 monolayers (ML) and three-dimensional or island-like growth thereafter.[2] The growth of Si on Ge is in the Volmer–Weber mode, which is pure three-dimensional growth.[3] Surfactant mediated epitaxy (SME) using As, Sb, Sn, Bi, and Te as surfactants has been used to grow thick, smooth and uniform Ge films on Si.[1,4–9]

For growing strained Si/Ge/Si heterostructures it is desirable that the Ge films be pseudomorphic with sharp interfaces. Low incorporation and easy removal of the surfactant is also important for any device applications. For growth temperatures between 400 and 500 °C, Bi is better suited as a surfactant over others. Bi has very low solubility in Si and Ge and it can be easily desorbed after the growth by a mild annealing.[8]

Herein, we report the study of strain and morphology of pseudomorphic Si/Ge heterostructures grown on Si (001) with Bi as a surfactant, using a combination of grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity. Williams *et al.* have studied the relaxation of Ge on Si(001), without a surfactant by *in situ* GIXD.[10] They also did similar studies using Sb as a surfactant.[5] Ge layers buried in a Si matrix have also been studied with GIXD by Headrick *et al.*[11] GIXD probes layers close to the surface and is very sensitive to the in-plane lattice spacing of the sample and thus can reveal strain information even in very thin films. X-ray reflectivity is sensitive to the electron density profile along the depth and therefore reveals information about the surface and interface roughness and film thickness.

II. EXPERIMENT

The samples were prepared by molecular beam epitaxy (MBE) in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The Si(001) substrates were degreased and Shiraki etched before being introduced into the chamber. Samples were then out-gassed for at least 12 h at 650 °C and then flash annealed at 950 °C to achieve a clean Si (001) surface, which was verified by a sharp two-domain 2×1 low-energy electron diffraction (LEED) pattern. No oxygen or carbon contamination of the surface was observed by Auger electron spectroscopy (AES). Samples were prepared with and without Bi as a surfactant with Ge coverages ranging from 1 to 10 ML. Throughout the growth, the temperature of the sample was held at 400 °C. For SME growth, initially a ML of Bi was deposited and then Ge deposition was carried out at a rate of 0.06 ML/min by evaporation

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TABLE I. Sample x-ray reflectivity fit parameters using the model shown in the inset of Fig. 4. t_{Si}=Si cap thickness, t_{Ge}=Ge layer thickness, $t_{oxide}\sim 25$Å.

No.	Sample description	t_{Si}(Å)	t_{Ge}(Å)	σ_{int}(Å)	σ_{surf}(Å)
1	10.0 ML of Ge without Bi	⋯	⋯	⋯	⋯
2	1.7 ML of Ge with Bi	⋯	⋯	⋯	⋯
3	7.1 ML of Ge with Bi	106.18	10.35	3.20	5.19
4	10.0 ML of Ge with Bi	144.01	14.53	11.53	6.35

from a Knudsen cell. During the Ge growth a constant overpressure of Bi was maintained to compensate for the desorption of Bi. After Ge deposition was complete Si deposition was carried out at a rate of about 1 ML/min from an e-beam evaporator. The Bi flux was turned off after 20 ML deposition of Si. The nominal thickness of the deposited Si was typically 100 Å. Non-SME growth conditions were identical except no Bi was used. The absolute Ge coverage of each sample was measured by a Ge K fluorescence comparison with a standard sample that was calibrated by Rutherford backscattering. At each stage of the film deposition the surface was studied by LEED and AES at room temperature. A total of four samples were prepared for this experiment. Sample 1 was prepared without Bi and had a measured Ge coverage of 10.0 ML. Samples 2–4 were prepared with Bi as a surfactant and had measured Ge coverages of 1.7, 7.1, and 10.0 ML, respectively (see Table I).

The x-ray measurements were performed at the Advanced Photon Source on a psi-circle diffractometer[12] at beamline 5ID-C and a four-circle diffractometer at beamline 2BM-B. A Si (111) monochromator was used to select a x-ray energy of 11.00 keV. A platinum coated flat mirror was used to filter out the higher harmonic photons from the x-ray beam. The slits on the detector arm were set to give an angular resolution of 1 mrad. Figures 1–3 show the collected scattered intensities for GIXD radial scans in the [110] direction passing through the (22L) rod (see the inset in Fig. 1). Each scan was performed at a fixed value of L corresponding to an angle near the critical angle ($\alpha_c = 0.16°$) for total-external x-ray reflection from Si at 11 keV. The exit angle was equal to the incident angle. Under this scattering geometry the x-ray scattering depth (Λ) is approximately half of the x-ray penetration depth[13] and is depicted as a function of L in the inset of Fig. 3. For radial scans at $L = 0.01$ the evanescent wave effect dramatically reduces the scattering depth to $\Lambda = 20$ Å, thus causing the scattered intensity to be originating entirely from the 100 Å Si cap layer. Above the critical angle, at $L = 0.04$, $\Lambda \sim 3000$ Å and there the scattered intensity has contributions from the substrate, Ge layer and the Si cap layer. This ability of GIXD to probe the in-plane lattice parameter at various depths makes it possible to estimate the strain in both the buried Ge layer and the Si cap layer. Specular x-ray reflectivity measurements (see Fig. 4) were also performed to estimate the surface and the interface roughness, and the thickness of the Ge and Si cap layers.

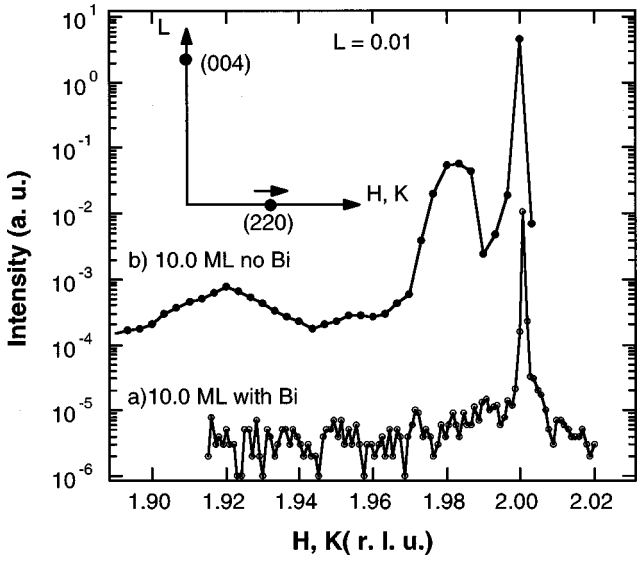

FIG. 1. *H,K* scans through (2 2 *L*), with $L = 0.01$ for Si/Ge layers with (a) 10.0 ML of Ge grown with Bi and (b) 10.0 ML of Ge grown without Bi. The scans are shifted vertically for clarity. The inset represents the scanning in reciprocal space.

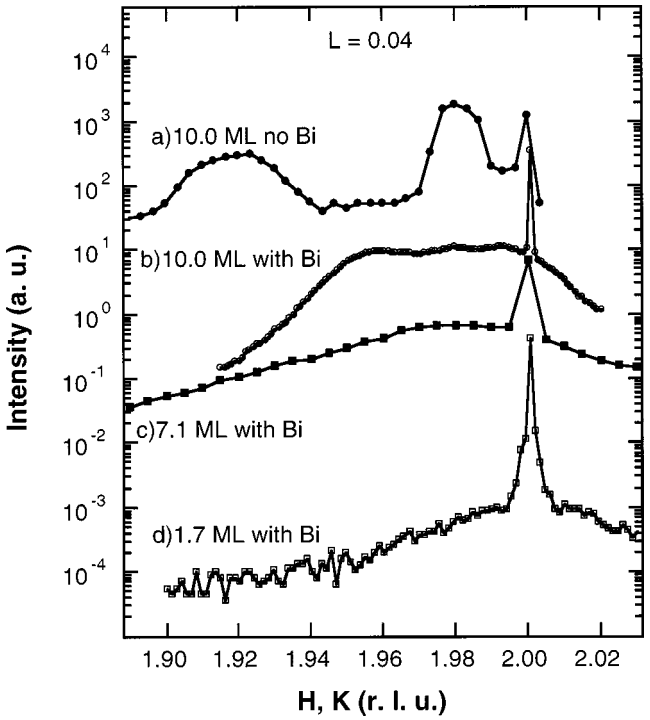

FIG. 2. *H,K* scans though (2 2 *L*), with $L = 0.04$ for (a) 10.0 ML Ge without Bi, (b) 10.0 ML Ge with Bi, (c) 7.1 ML Ge with Bi, and (d) 1.7 ML Ge with Bi. The scans are shifted vertically for clarity.

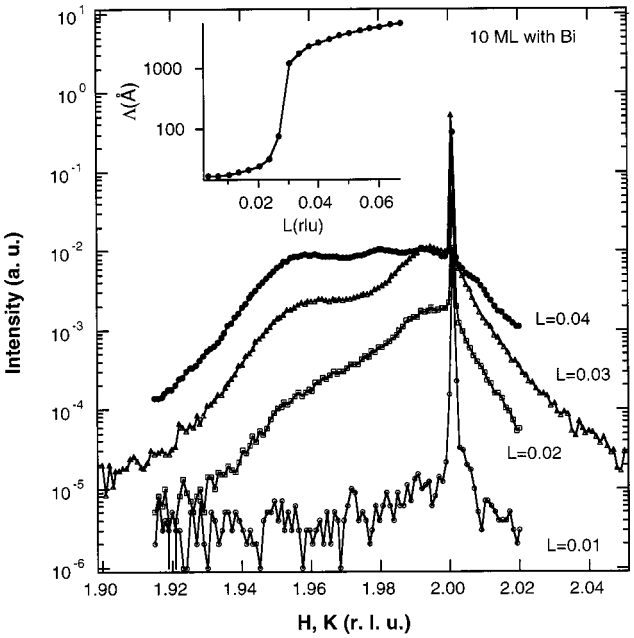

FIG. 3. *H,K* scans through (2 2 *L*), with various values of *L* for sample with 10.0 ML of Ge with Bi. The scans are shifted vertically for clarity. The calculated x-ray scattering depth as a function of *L* is shown in the inset.

III. RESULTS AND DISCUSSION

The *in situ* LEED and Auger surface analysis indicated that Bi segregated to the surface at all times during the MBE growth. The surface reconstruction of Bi on Si (001) is coverage dependent.[14,15] The LEED pattern after Bi deposition on Si at 400 °C was two-domain $(2\times n)$ with *n* equal to 4 or 5. The saturation coverage is then equal to $(n-1)/n$ ML[14,16]

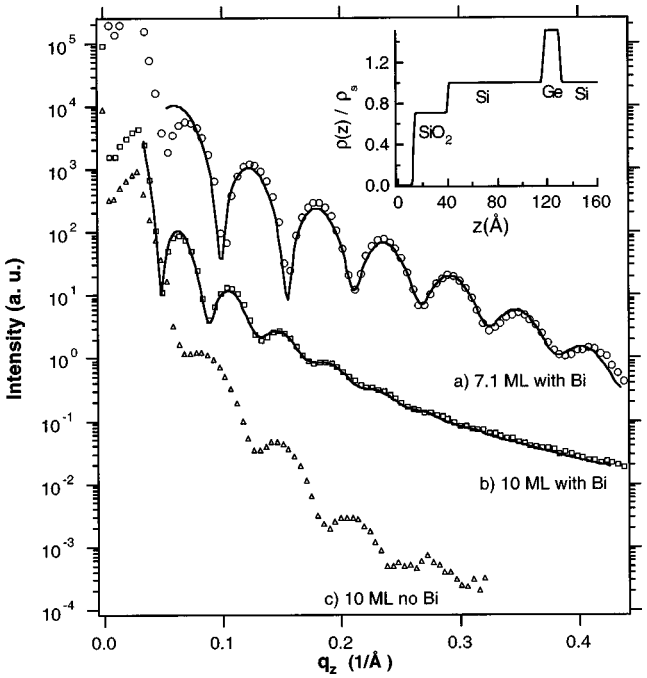

FIG. 4. Reflectivity data (points) and model fit (line) for (a) 7.1 ML with Bi, (b) 10.0 ML with Bi, and (c) 10.0 ML without Bi. The scans are shifted vertically for clarity. The electron density profile relative to Si used to fit the data is shown in the inset.

which is approximately 0.8 ML. On Bi surfactant samples, the LEED pattern after Ge deposition was $2\times n$ with *n* varying between 2 and 5. The decrease in *n* can be explained by Bi desorption. The LEED observations were similar after the deposition of the Si cap layer, however the spots were more diffuse. Using AES no Ge was detected on the surface after Si deposition. This clearly shows that Bi segregated to the Ge growth surface and to the Si growth surface.

For normal Ge growth without Bi, the Ge surface reconstruction was 2×1 during two-dimensional (2D) growth. For sample 1 after 10 ML of Ge deposition we observed a LEED pattern that had additional spots consistent with the three-dimensional (3D) growth of Ge pyramid shaped islands with {105} facets.[17,18] After depositing the Si cap layer a diffuse 2×1 LEED pattern was observed and traces of Ge were detected by AES. Part of the Ge thus diffused into the Si layer and segregated to the surface, when Bi was not used as a surfactant.

Figure 1 shows the *H, K* scans at $L=0.01$ for the 10 ML Ge samples with (a) and without (b) Bi. The x-ray scattering depth was approximately 20 Å, ensuring that only the top layers in the Si cap layer were probed. For the 10 ML sample with Bi there was only one peak at the $(2\ 2\ L)$ Si bulk position indicating that the Si cap layer was of very high crystallinity. For the 10 ML sample without Bi there were two additional peaks one at *H, K* = 1.92 that corresponds to a relaxed Ge layer and another at *H, K* = 1.98 from a Si–Ge alloy.

Figure 2 shows the *H, K* scans for all four samples at $L=0.04$, where the x-ray scattering depth is ~3000 Å. Therefore all the layers were probed with contribution to the scattered x-ray intensity decreasing with depth due to absorption. For 10 ML without Bi, the two scans in Figs. 1 and 2 had the same three peaks, with the relaxed Ge peak at *H, K* = 1.92 increasing in relative intensity as the scattering depth was increased. As seen in Fig. 2 the 7.1 ML Ge film grown with Bi was still pseudomorphic as no scattering was observed at the Ge bulk position of *H, K* = 1.92. For 10 ML Ge film grown with Bi the broad peak in between the Ge and Si bulk positions indicates that the Ge atomic layers were partially relaxed. For a Ge coverage of 1.7 ML the film was found to be completely pseudomorphic. To probe the strain relaxation in the Si/Ge heterostructure as a function of depth we performed additional scans at $L=0.02$ and 0.03 for 10 ML sample with Bi, as shown in Fig. 3. These scans clearly showed the nonuniform nature of the strain.

The x-ray specular reflectivity measurements in Fig. 4 were compared to the electron density profile model shown in the inset of Fig. 4. An additional 20–25 Å silicon–oxide layer on top of the Si cap layer had to be included in the model to fit the data properly. Table I reports the best-fit values obtained by the chi-squared fitting of the modeled reflectivity to the data. Using the model shown it was not possible to fit the reflectivity curve for 10 ML sample without Bi as it had both 2D and 3D structures. For the 10 ML Ge films the one grown with Bi clearly has sharper interfaces as seen from the oscillations. The 7.1 ML film grown with Bi has less roughness and sharper interfaces than the 10 ML sample with Bi.

Our conclusions for the Ge grown on Si(001) without Bi as a surfactant are as follows. Layer-by-layer growth of Ge proceeds up to 3 ML and thereafter island formation begins to relieve the strain in the Ge layer. These islands were faceted with {105} planes. The peak at H, $K=1.92$ was from the Ge layers at the top of the islands which were completely relaxed. Ge segregated in Si and therefore Si growth on Ge resulted in Ge diffusing into the Si layer and the formation of a Si–Ge alloy. This alloy had a lattice constant in between Si and Ge which gave rise to the peak at H, $K=1.98$. The formation of Ge islands and the Ge–Si intermixing resulted in a very rough and diffuse interface.

For the Bi surfactant mediated epitaxy case, Bi segregated strongly in both the Ge and Si layers. Due to its size and lower surface free energy Bi was not easily incorporated into the film. Bi inhibited the diffusion of Ge atoms along the surface, which resulted in layer-by-layer pseudomorphic growth of Ge up to 7 ML. This is equivalent to that reported by LeGoues *et al.* for the case of As as a surfactant,[4] while Thornton *et al.* measured *in situ* ~11 ML of pseudomorphic Ge growth using Sb as a surfactant before the onset of strain relaxation.[5] At 10 ML of Ge, the film with Bi was only partially relaxed. In Fig. 3 at $L=0.02(\Lambda\sim 30\,\text{Å})$ a weak broad peak appeared at H, $K=1.99$. The intensity of this peak increased further at $L=0.03(\Lambda\sim 900\text{Å})$. The absence of such a peak for 1.7 ML of Ge with Bi rules out any intermixing of Ge and Si. We thus infer that the Si atomic layer at the bottom of the cap close to the Si/Ge interface had an in-plane lattice spacing that is about 0.05% larger than bulk Si. This strain in the Si cap layer at the Si–Ge interface is due to the fact that the underlying Ge had partially relaxed. The presence of Bi on the surface again prevented Ge diffusion and made Si grow layer-by-layer. In contrast to the Si/10 ML Ge structure grown without Bi, no alloying was observed for the Si/Ge SME samples. The partially relaxed Ge layer also made the interface rough as seen in the reflectivity measurements. For the SME grown structures the film roughness increased considerably from 7 to 10 ML. Roughening increased the surface area and allowed the top Ge layer to partially relax. Interface roughening thus can achieve partial strain relief where island formation is kinetically inhibited.

IV. CONCLUSIONS

In summary we studied, in the pseudomorphic regime, the strain, and morphology of Si/Ge heterostructures grown using surfactant mediated MBE with Bi as the surfactant. Using LEED, AES, GIXD, and x-ray reflectivity we observed that Bi segregated to the growth surface, prevented segregation of Ge in Si and promoted layer by layer growth. We found that up to 7 ML of pseudomorphically strained Ge can be grown on Si (001) with Bi. Our measurements indicate that at 10 ML the Ge layers grown with Bi were partially relaxed and strained the Si cap layer. We observed that Ge films grown with Bi as a surfactant undergo partial relaxation by increasing the roughness of the Ge–Si interface.

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[1] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[2] M. Asai, H. Ueba, and C. Tatsuyama, J. Appl. Phys. **58**, 2577 (1985).
[3] K.-N. Tu, J. W. Mayer, and L. C. Feldman, *Electronic Thin Film Science for Electronic Engineering & Material Science* (Macmillan, New York, 1992), p. 167.
[4] F. K. LeGoues, M. Copel, and R. M. Tromp, Phys. Rev. B **42**, 11690 (1990).
[5] J. M. C. Thornton, A. A. Williams, J. E. Macdonald, R. G. van Silfhout, M. S. Finney, and C. Norris, Surf. Sci. **273**, 1 (1992).
[6] X. W. Lin, Z. L-Weber, J. Washburn, E. R. Weber, A. Sasaki, A. Wakahara, and T. Hasegawa, J. Vac. Sci. Technol. B **13**, 1805 (1995).
[7] K. Sakamoto, K. Kyoya, K. Miki, H. Matsuhata, and T. Sakamoto, Jpn. J. Appl. Phys., Part 2 **32**, L204 (1993).
[8] T. Schmidt, J. Falta, G. Materlik, J. Zeysing, G. Falkenberg, and R. L. Johnson, Appl. Phys. Lett. **74**, 1391 (1999).
[9] S. Higuchi and Y. Nakanishi, J. Appl. Phys. **71**, 4277 (1992).
[10] A. A. Williams, J. M. C. Thornton, J. E. Macdonald, R. G. van Silfhout, J. F. van der Veen, M. S. Finney, A. D. Johnson, and C. Norris, Phys. Rev. B **43**, 5001 (1991).
[11] R. L. Headrick, J.-M. Baribeau, D. J. Lockwood, T. E. Jackman, and M. J. Bedzyk, Appl. Phys. Lett. **62**, 687 (1993).
[12] P. F. Lyman, D. T. Keane, and M. J. Bedzyk, in *Synchrotron Radiation Instrumentation*, edited by Ernest Fontes, AIP Conf. Proc. No. 417 (AIP, Woodbury, NY, 1997), pp. 10–14.
[13] H. Dosch, B. W. Batterman, and D. C. Wack, Phys. Rev. Lett. **56**, 1144 (1986).
[14] T. Hanada and M. Kawai, Surf. Sci. **242**, 137 (1991).
[15] Y. Qian, M. J. Bedzyk, P. F. Lyman, T.-L. Lee, S. Tang, and A. J. Freeman, Phys. Rev. B **54**, 4424 (1996).
[16] P. F. Lyman, Y. Qian, T.-L. Lee, and M. J. Bedzyk, Physica B **221**, 426 (1996).
[17] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).
[18] A. J. Steinfort, P. M. L. o. Scholte, A. Ettema, F. Tuistra, M. Nielsen, E. Landemark, D.-M. Smilgies, R. Feidenhans'l, G. Flkenberg, L. Seehofer, and R. L. Johnson, Phys. Rev. Lett. **77**, 2009 (1996).