

Interface-Mixing in Ge Heteroepitaxy on Si(001): Microscopic Mechanism

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The role of surface strain in interface mixing during molecular beam epitaxy (MBE) growth of Ge and Si on Si(001) has been studied by *surface-sensitive* X-ray absorption fine structure (XAFS). The effect of Bi surfactant on interface mixing was studied by the radial distribution around Ge atoms in Ge/Si heterointerfaces. It was found that Bi surfactants can dramatically suppress interface mixing based on two pathways of migration along the growth direction, *i.e.*, surface segregation and the interchange with substrate. The results indicate that the surface strain opens up layer- and site-specific migration channels between the second and third layers. Possible microscopic mechanism of interface mixing induced by surface strain is proposed.

1. INTRODUCTION

Strained-layer superlattices (SLs) with a very short period attract much attention as a new class of materials with exotic properties such as new optical transitions observed for Ge_4Si_4 SLS on Si(001).¹⁾ For these materials, the role of heterointerface is crucial in understanding their physical properties. In particular, chemical order and strain are expected to strongly influence the electronic states and oscillator strengths for optical transition. X-ray absorption fine structure (XAFS) studies for Ge_n/Si heterostructures ($n < 7$)²⁾ demonstrated the interface mixing associated with molecular beam epitaxy (MBE) growth. However, the magnitude of intermixing which can not be explained by a simple thermal diffusion mechanism has been a puzzling problem. In the present study, the effect of Bi surfactant on interface mixing has been studied by extended X-ray absorption fine structure (EXAFS).

2. EXPERIMENTAL

The Ge K-edge XAFS spectra were obtained from the Ge $K\alpha$ fluorescence yield in a surface sensitive geometry using a 7-element Si(Li) detector and a 27-pole wiggler magnet at the Photon Factory. The Si and Ge layers were grown by a MBE technique on a well-oriented p-type Si(001) (4 ohm-cm) surface at 400°C. The oscillatory intensities of reflection high energy electron diffraction (RHEED) during the growth of Si and Ge layers taken from the [010] azimuth were utilized to control the number of Si and Ge layers. Surface-sensitivity in the order of *ca.* 0.1 ML has been achieved by combining a grazing incidence geometry with an energy analysis of fluorescence spectrum.³⁾ The effect of Bi surfactant on interface mixing was studied by the Ge K-EXAFS for $\text{Si}_{30}/\text{Ge}_4/\text{Si}$ samples grown with and without Bi surfactant. A sample grown without Bi

without Bi surfactant. A sample grown without Bi surfactant is denoted as $\text{Si}_{30}/\text{Ge}_4/\text{Si}$ while $\text{Si}_{30}/\text{Ge}_4/\text{Bi}/\text{Si}$ and $\text{Si}_{30}/\text{Bi}/\text{Ge}_4/\text{Si}$ refer to two samples grown with Bi surfactant on Si substrate and on Ge overlayers, respectively.

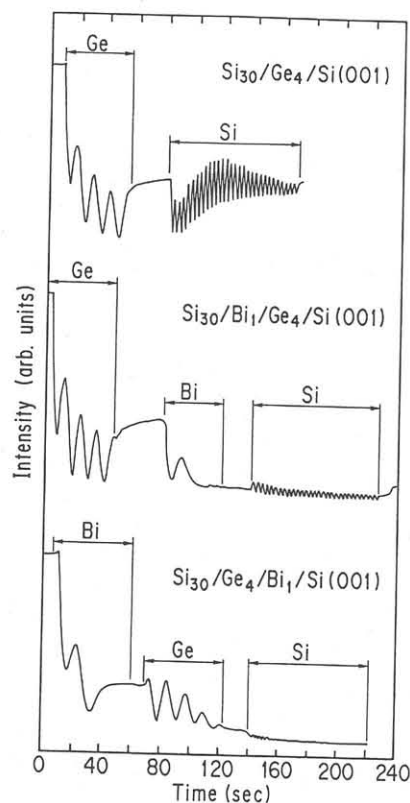


Fig. 1 RHEED intensity oscillations during the growth of $\text{Si}_{30}/\text{Ge}_4/\text{Si}$ heterostructures by MBE.

3. RESULTS AND DISCUSSION

Figure 1 show the variation of RHEED intensity during the growth of Si₃₀/Ge₄/Si heterostructures by MBE. The magnitude of RHEED oscillation during the growth of 30 ML Si decreases when 1 ML Bi is adsorbed prior to Si growth, indicating that the surface is roughened because the migration of Si adatoms is suppressed. Roughening is most significantly observed for Si₃₀/Ge₄/Bi/Si. The nearest-neighbor Ge K-EXAFS oscillations for Si₃₀/Ge₄/Si, Si₃₀/Bi/Ge₄/Si and Si₃₀/Ge₄/Bi/Si are compared together with those for Si₃₀/Ge₁/Si and Ge_{0.5}Si_{0.5} alloy in Fig. 2. The envelope of oscillation provides the information on atomic species since the k-dependence of backscattering amplitudes for Ge and Si are substantially different: the

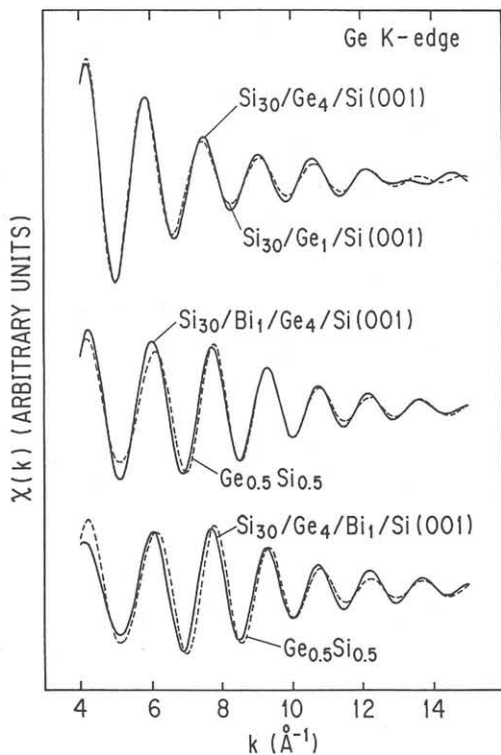


Fig. 2 First-shell Ge K-EXAFS oscillations for the Si/Ge₄/Si, Si/Ge₄/Bi/Si and Si/Bi/Ge₄/Si together with those for Si₃₀/Ge₁/Si(001) and Ge_{0.5}Si_{0.5}.

backscattering amplitude $|f_i(\pi, k)|$ for Si atom peaks at low k and falls off sharply with the increase of k while $|f_i(\pi, k)|$ for Ge atom has a maximum at $k = 6-7 \text{ \AA}^{-1}$ and extends to $k > 15 \text{ \AA}^{-1}$.

The ratio of the number of Ge-Si pairs to the Ge-Ge pairs (N_{Si}/N_{Ge}) and bond lengths, R_{GeGe} and R_{GeSi} , were determined by a least-squares curve fit. It is found that the $N_{Si}/N_{Ge} \gg 1$ for Si₃₀/Ge₄/Si and $N_{Si}/N_{Ge} \sim 1$ for Si₃₀/Ge₄/Bi/Si and Si₃₀/Bi/Ge₄/Si. N_{Si}/N_{Ge} can be a measure of intermixing: $N_{Si}/N_{Ge} = 0.75$ for Si/Ge₄/Si with an ideal interface increases as the degree of interface mixing increases. It was found that the nearest-neighbors of Ge atoms in

Si₃₀/Ge₄/Si and Si₃₀/Ge₁/Si are mostly Si atoms. This indicates that the migration of Ge atoms extends beyond three MLs. The interface mixing is dramatically suppressed by Bi surfactant.⁴⁾ Further, interface mixing in Si₃₀/Ge₄/Bi/Si is less prominent than in Si₃₀/Bi/Ge₄/Si. The difference between the two samples is roughly equal to the contribution of site exchange with substrate Si. Bi adsorption on Si reduces the two interface mixing channels, i.e., surface segregation during Si growth on Ge and site exchange between Ge and substrate Si.

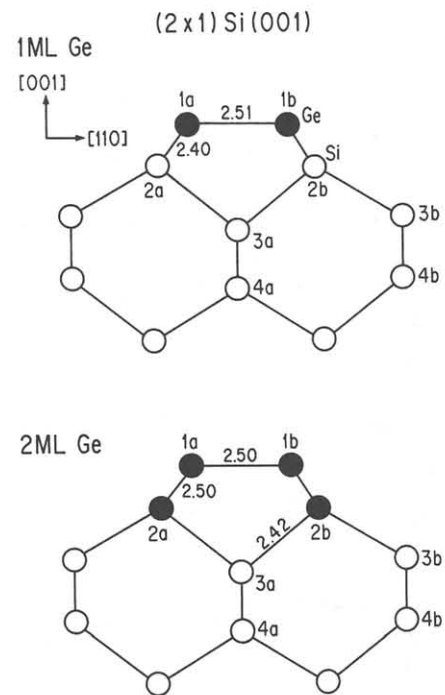


Fig. 3 Structures for 1 ML Ge and 2 ML Ge on Si(001).

Figure 3 shows the local structures observed for 1 ML and 2 ML Ge overlayers on Si(001).³⁾ Elongated R_{GeGe} and shortened R_{GeSi} effectively increases the bond length mismatch to 10%, much larger than the conventionally used lattice mismatch value (4%). The strain in the second layer would sharply increase when they are occupied by Ge atoms. Possible channels of atomic migration which would reduce the elastic strain are indicated by arrows. In Fig. 3, sites 2a, 2b and 3a are under compressive strain while site 3b is under tensile strain.

For 2 ML Ge, both compressive strain at site 2b and tensile strain at site 3b increase. The second layer sites (2a, 2b) are thus unfavorable for Ge atoms and the channels of atom migration connecting these sites (2b-3b, 2a-3a) would open up. The curve fit analysis of EXAFS data 1 ML and 2 ML Ge on Si(001) indeed indicated that the second layer Ge atoms are replaced with Si atoms in the third layer.³⁾ This mechanism can be applied to a surface segregation of Ge atoms observed during Si growth on Ge which predominates the interface mixing. Bi adsorption removes the surface

strain due to the surface reconstruction, which suppresses the strain-induced "Ge pump" mechanism.⁵⁾ If Bi adsorption takes place on Si, two pathways of interface mixing, *i.e.*, surface segregation and site exchange at the interface are prohibited.

Figure 4 schematically illustrates the effect of Bi surfactant on interface mixing. In this mode, the surface strain is a dominant driving force of atomic migration through specific channels between the second and third layers. 1 ML Bi adsorption reduces the surface strain

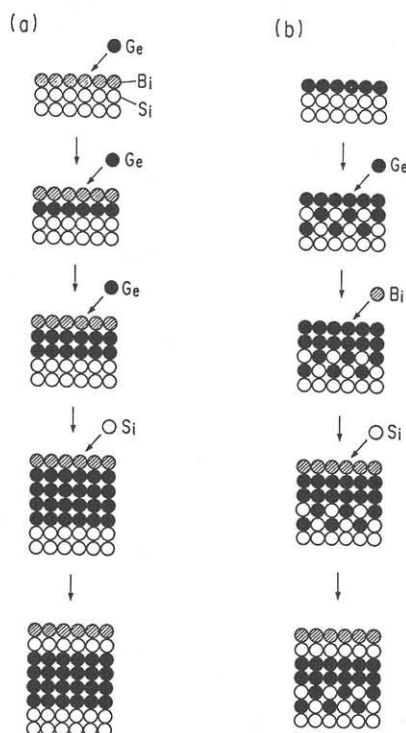


Fig. 4 Schematic for the interface-mixing in the Si/Ge/Si heteroepitaxy using Bi surfactant (a) Si/Ge₄/Bi/Si and (b) Si/Bi/Ge₄/Si.

due to surface reconstruction. Upon the growth of 1 ML Si on the Ge overlayers, the Ge atoms in the second layer are subjected to a large surface strain. It is expected that Ge atoms would interchange with Si atoms in the first layer through channels (1a,b-2a,b). These channels serve as a driving force of the surface segregation and site exchange.

The contribution of site exchange estimated from the difference between the N_{Ge} values for Si₃₀/Ge₄/Bi/Si and Si₃₀/Bi/Ge₄/Si is *ca.* 0.4 ML. This value is close to the observed value *ca.* 0.5 ML for 2 ML Ge on Si(001)³⁾. If we assume that the second layer Ge atoms are replaced by Si adatoms, the total number of Ge atoms involved in interface mixing would be *ca.* 1.5 MLs. The observed total number of interchanged Ge atoms was *ca.* 2 MLs. This suggests that the mechanism of strain-induced intermixing extends beyond the third nearest neighbors. Such a medium-range intermixing is observed for the III-V interfaces.⁶⁾

4. SUMMARY

From a direct measurement of nearest neighbor species of Ge atom, the effect of Bi surfactant on interface mixing has been studied on a microscopic scale. It was found that Bi adsorption prior to the growth of Ge and Si drastically inhibits the interface mixing via surface segregation and interchange with Si substrate. The in-situ XAFS results show that there exist layer- and site-specific channels of atom migration induced by surface strain. The role of Bi surfactant is ascribed to the elimination of surface strain which arises from surface reconstruction and atom size effect.

REFERENCES

- 1) T.P. Pearsall, J. Bevk, L.C. Feldman, J.M. Bonar and J.P. Mannaerts: Phys. Rev. Lett. 58 (1987) 729.
- 2) H. Oyanagi, K. Sakamoto and T. Sakamoto: Jpn. J. Appl. Phys. 32 (1993) 119.
- 3) R. Zachai, E. Frieess, G. Abstreiter, E. Kasper and H. Kibbel: Phys. Rev. Lett. 64 (1990) 1055.
- 4) U. Menezigar, J. Brunner, E. Frieess, M. Gail, G. Abstreiter, H. Kibbel, H. Presting and E. Kasper: Thin Solid Films, 222 (1992) 227.
- 5) H. Oyanagi, K. Sakamoto, R. Shioda and K. Sakamoto, Jpn. J. Appl. Phys. 33 (1994) 3545.
- 6) Y. Kuwahara, H. Oyanagi, R. Shioda, Y. Takeda, H. Yamaguchi and M. Aono: Jpn. J. Appl. Phys. in press.