Atomistic evolution of $Si_{1-x-y}Ge_xC_y$ thin films on Si(001) surfaces

Akira Sakai,[a] Yuji Torige, Masahisa Okada, Hiroya Ikeda, and Yukio Yasuda
Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Shigeaki Zaima
Center for Cooperative Research in Advanced Science and Technology, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

(Received 5 June 2001; accepted for publication 4 September 2001)

The initial growth process of $Si_{1-x-y}Ge_xC_y$ thin films on Si(001) surfaces is examined by scanning tunneling microscopy. The surface morphology of the film critically depends on the C fraction in the film. Evidence is presented on an atomic scale that the epitaxial growth of $Si_{1-x-y}Ge_xC_y$ films with large C fractions is dominated by phase separation between Si–C and Si–Ge, concomitant with C condensation on the surface of the growing films. We find that the addition of a thin (1–2 ML) SiGe interlayer between the $Si_{1-x-y}Ge_xC_y$ film and the Si substrate drastically improves the film structure, leading to a planar morphology even with large C fractions present in the film. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1418447]

The ternary $Si_{1-x-y}Ge_xC_y$ alloy system has recently attracted considerable attention due to the potential for electronic and optoelectronic device applications based on heterojunctions made of group IV elements.[1] The incorporation of C atoms into $Si_{1-x}Ge_x$ films offers the possibility of compensation of compressive strain due to the much smaller covalent radius of C compared to Si. Extensive research has been also carried out to reveal the detailed band alignment of $Si_{1-x}C_x$/Si and $Si_{1-x-y}Ge_xC_y$/Si heterostructures.[2–4] The charge transport properties have been carefully examined in the course of applying these systems as active layers in electronic devices.[1,5]

The crystalline quality of $Si_{1-x-y}Ge_xC_y$ epitaxial films on Si is of particular importance with regard to their electronic and optical properties. In contrast to the entirely miscible Si–Ge system, the equilibrium solid solubility of C in bulk Si is less than the order of 10^{18} atoms/cm^3 at the melting point.[6] Although an enhanced solubility of C on Si(001) surfaces has been reported,[7] the incorporation of substitutional C at large fractions is still somewhat limited. In general, C fractions exceeding a few percent result in a degradation of the film morphology, which appears as surface roughening, the formation of extended defects or the precipitation of SiC phases. Although there have been several previous attempts to grow high crystalline-quality $Si_{1-x-y}Ge_xC_y$ films and to clarify the behavior of C atoms with respect to their influence on the growth mode,[8,9] the microscopic understanding of the mechanism of $Si_{1-x-y}Ge_xC_y$ film evolution is not sufficiently understood at present. In this letter, through scanning tunneling microscopy (STM) analysis of $Si_{1-x-y}Ge_xC_y$ films formed on Si under various conditions, we investigate the atomistic mechanisms present during the initial stage of the film evolution. Our atomic scale observations clarify the occurrence of phase separation between Si–C and Si–Ge and of C condensation on the surface of growing films. We successfully demonstrate a simple but effective procedure to lead to high crystalline quality of films even with large C fractions.

A molecular beam epitaxy system equipped with an electron beam evaporator for Si, a pyrolytic boron nitride Knudsen cell for Ge, and a sublimation source for C was used in the experiment. The C deposition was performed by passing a direct current through a graphite filament. The growth rate of C was calibrated by measuring directly the amount of C deposited on a Si surface at room temperature using a STM observation. A Si(001) sample (p type, 3 Ω cm) was thermally cleaned at 1150 °C for several minutes by direct current heating. The sample was then cooled to 600 °C in order to perform the growth experiments. In this experiment, the fluxes of Si and Ge were chosen to be in the ratio of 1:1 and only the C fraction was changed. After the $Si_{1-x-y}Ge_xC_y$ film growth the sample was quenched to room temperature and transferred to the STM chamber under ultrahigh vacuum conditions. The STM images were measured with a typical sample bias of -2.0 V.

First, we look at the STM results obtained for $Si_{1-x}Ge_x$ films. Figure 1(a) shows the surface morphologies of $Si_{0.5}Ge_{0.5}$ films, which are dependent on the film thickness. As expected, it can be clearly seen that a $(2\times n)$-ordered missing dimer structure[10] was formed on the surface, which results from the strain relief of compressed $Si_{1-x}Ge_x$ films. As the film thickness increases, two-dimensional islands were frequently formed on the terraces, as shown in Fig. 1(b). We also find an enhanced undulation of S_B step edges[11] which align approximately parallel to the missing dimer row, alternating with relatively straight S_A steps. This undulation forms characteristic domains that protrude from the straight S_A step edge and elongate along the direction perpendicular to their inherent missing dimer rows. The fact that S_B step undulation occurs in the compressive-stressed film is quite unique, compared with the previous results for Ge/Si(001) systems where S_A step undulation preferentially occurs due to a reversal of the surface stress anisotropy.[12,13] A closer inspection of the STM images reveals that the S_A steps bounding the elongated domain are connected by missing

[a]Electronic mail: sakai@alice.xtal.nagoya-u.ac.jp

 © 2001 American Institute of Physics
Downloaded 18 Oct 2006 to 133.6.32.11. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

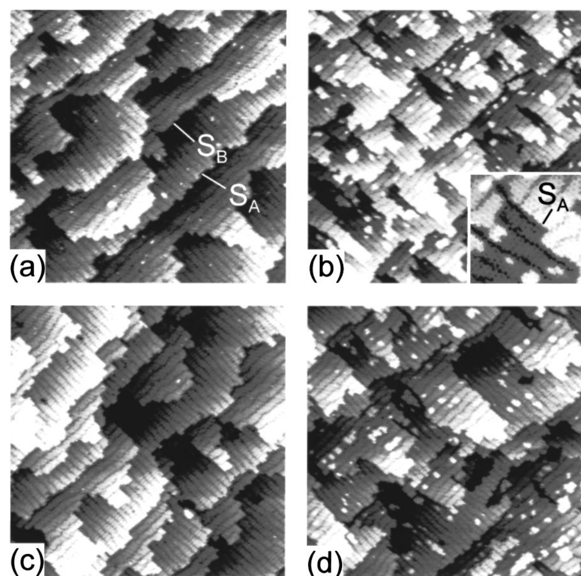

FIG. 1. STM images (100×100 nm^2) of the surface structure of $Si_{0.5}Ge_{0.5}$ films at (a) 6 ML and (b) 8 ML thickness and of $Si_{0.489}Ge_{0.489}C_{0.022}$ films at (c) 6 ML and (d) 8 ML thickness. All the samples were grown on Si(001) substrates at 600 °C. The magnified inset in (b) shows the connection between S_A steps by missing dimer rows underneath and the kink structure.

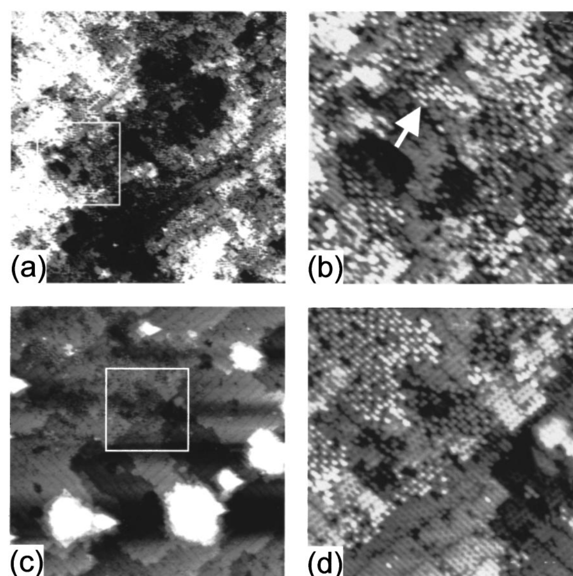

FIG. 2. STM images (100×100 nm^2) of $Si_{0.478}Ge_{0.478}C_{0.044}$ films at (a) 3 ML and (c) 4 ML thickness. (b) and (d) are magnified 30×30 nm^2 images of the boxed area in (a) and (c), respectively. An example of the $c(4\times4)$ reconstruction is indicated by the arrow in (b).

dimer rows running underneath [see magnified inset in Fig. 1(b)]. Furthermore, they are shown to have kinks with a length approximately n times the unit of the $(2\times n)$ reconstruction. Therefore, it is likely that the S_A steps connected with the missing dimer rows play an essential role in relieving the compressive strain in the films.

On the other hand, as shown in Figs. 1(c) and 1(d), $Si_{0.489}Ge_{0.489}C_{0.022}$ films also exhibit a $(2\times n)$ reconstructed surface and the S_B step undulation forms elongated domains similar to the $Si_{1-x}Ge_x$ case, especially in thicker films. A noticeable difference between the two surfaces of the $Si_{1-x}Ge_x$ and $Si_{1-x-y}Ge_xC_y$ films is reflected in the separation between adjacent domains, which is measured perpendicular to the elongated direction. Comparing two such films having the same thickness, the domains on the $Si_{1-x-y}Ge_xC_y$ film surface have a longer separation on average than those on the $Si_{1-x}Ge_x$ film surface. According to a theoretical treatment given by Alerhand *et al.*,[14] this separation, l, is correlated with the elastic relaxation energy $E_{\rm el}$ in the form of $E_{\rm el}\propto 1/l\cdot\log_e(l/\pi a)$, where a is the surface lattice constant. From this formula, we can estimate the contribution of surface steps to the strain energy relaxation in the film. Comparing the $E_{\rm el}$ values obtained from an average separation of ~12 nm for the $Si_{1-x}Ge_x$ film and ~18 nm for $Si_{1-x-y}Ge_xC_y$, we find in the $Si_{1-x-y}Ge_xC_y$ film approximately a 22% reduction in the step contribution to the strain energy relaxation, relative to that in the $Si_{1-x}Ge_x$ film. In other words, C atoms incorporated into the film explicitly play a role in compensating the compressive strain.

Figure 2 shows the surface of a $Si_{1-x-y}Ge_xC_y$ film with a C fraction of 4.4%. As is clearly observed in Fig. 2(a), every step is heavily perturbed and prominent surface roughening occurs even at a thickness of 3 ML, which is much thinner than that in the case in Fig. 1. Figure 2(b) shows an atomic resolution scan of the boxed area in Fig. 2(a). Elongated bright spots that are arranged into patches of a $c(4\times4)$ reconstructed structure are partially observed on the surface (see arrow). Structural models for the $c(4\times4)$ reconstruction are still a controversial subject[15] and the determination of these is beyond the scope of this letter. However, the observations suggest that the reconstruction is induced by the condensation and subsurface incorporation of surface C atoms. At 4 ML, as shown in Fig. 2(c), the surface exhibits the onset of three-dimensional (3D) islanding and the formation of fairly flat terraces bounded by single layer steps in other regions. The islands, with a height of about 2 nm on average, are frequently observed on top of protruding regions of the terraces. The apparent feature seen on the terrace is the $c(4\times4)$ reconstruction [see Fig. 2(d)] and the $(2\times n)$ reconstruction consisting of buckled dimers and missing dimer rows. From these results, we find that the growth does not proceed in a layer-by-layer manner and instead that significant C condensation on the growing surface starts at the initial stage of the film growth, resulting in a $c(4\times4)$ reconstruction. Furthermore, the fact that 3D islanding has taken place, even in films thinner than the small C fraction sample, indicates an increased Ge fraction locally around the island for which the film locally exceeds in the critical thickness for islanding. Since we have confirmed that at the very initial stages less than 2 ML a conformable surface morphology can be achieved without any islands, the islands observed here are not formed at the beginning of the growth, although there are several reports showing C-induced Ge island formation.[16] These results clearly show the formation of C-rich and Ge-rich regions in the film, which is presumably driven by the phase separation between Si–C and Si–Ge during growth when the film contains a high concentration of C. This may be reasonable in light of the fact that C is immiscible in bulk Ge.[17] A theoretical investigation[18] has also predicted that the interaction between Ge and C in the Si lattice is repulsive and this was later verified experimentally.[9] Our STM results corroborate this phenomenon and provide insight into the mechanism on an atomic scale.

Downloaded 18 Oct 2006 to 133.6.32.11. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

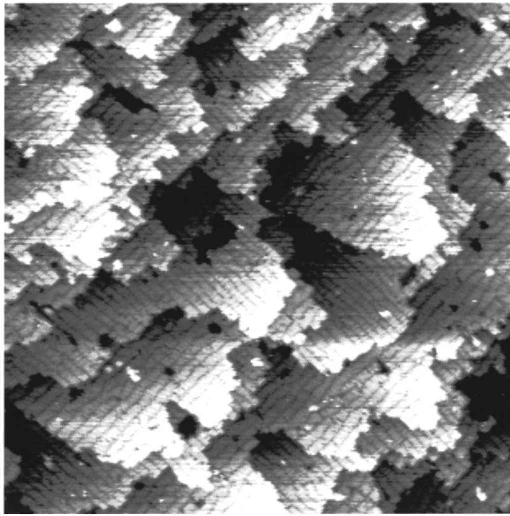

FIG. 3. STM image (140×140 nm^2) of a sample with a $Si_{0.473}Ge_{0.473}C_{0.054}$(6 ML)/$Si_{0.5}Ge_{0.5}$(1 ML)/Si(001) structure. Note that a planar surface morphology is formed in spite of the large C fraction.

It is obvious in the growth of films with larger C fractions that C condensation and phase separation simultaneously occur in the initial stages such that 3D islands are locally formed, leading to a deterioration of the film crystalline quality. In order to overcome this problem and to grow large-C-fraction-$Si_{1-x-y}Ge_xC_y$ films with a high crystalline quality, we have employed the use of a thin $Si_{1-x}Ge_x$ interlayer between the $Si_{1-x-y}Ge_xC_y$ film and a Si substrate. The samples were prepared by first depositing a $Si_{0.5}Ge_{0.5}$ layer of 1 or 2 ML on a clean Si surface at 600 °C and then growing a $Si_{1-x-y}Ge_xC_y$ film at the same temperature. Figure 3 shows a STM image of a sample that has the structure $Si_{0.473}Ge_{0.473}C_{0.054}$(6 ML)/$Si_{0.5}Ge_{0.5}$(1 ML)/Si(001). Note that a planar surface morphology was formed, even though the film had a large C fraction. Compared with the surface of the 4 ML-$Si_{0.478}Ge_{0.478}C_{0.044}$ film shown in Fig. 2(c), neither 3D islands nor $c(4\times4)$ reconstructions were observed, despite the larger total film thickness (7 ML) and average C fraction (4.6%). This clearly demonstrates that the $Si_{1-x}Ge_x$ interlayer explicitly plays a role in suppressing C condensation and phase separation during the film evolution.

From the above observation, we have found that a simple additional procedure of forming a $Si_{1-x}Ge_x$ interlayer drastically alters the subsequent growth process of $Si_{1-x-y}Ge_xC_y$ and remarkably improves the film quality. In order to deduce a mechanism by which the SiGe interlayer suppresses C condensation and phase separation, we have considered the possible chemical interactions among Si, Ge, and C in the growing film. Here, the Si–C attractive and the Ge–C repulsive interactions are dominant factors for determining the film evolution in Si–Ge–C systems. The former leads to C condensation, appearing as a $c(4\times4)$ reconstruction and the latter induces phase separation, resulting in 3D islanding. Therefore, it is of importance to consider the incorporation site for C atoms when growing a random alloy film of $Si_{1-x-y}Ge_xC_y$. Previous reports have shown that Si–Ge mixed dimers are predominant on a submonolayer-deposited Ge/Si(001) surface.[19] This means that Si and Ge atoms are almost randomly distributed on the surface. In our case, the same feature is presumably completed on the surface just after the formation of the $Si_{0.5}Ge_{0.5}$ interlayer on the clean Si surface. Now we consider the case of Si, Ge, and C fluxes deposited on that surface. Due to the chemical interactions between them, it is most likely that C atoms are preferentially adsorbed on to Si bonds and not absorbed on to Ge bonds. Since, in principle, the Si and Ge bonds are randomly distributed, the opportunity for the local condensation of C would appear to be very small. This mechanism allows the C atoms to be incorporated randomly in the film. Furthermore, we can confirm a surfactant-like behavior of the interlayer by the fact that a preformed layer determines the final film morphology on it. This strongly suggests the existence of a Ge–C site exchange on the growing surface, which might be due to the higher surface tension of C compared to Ge.[20] Although our model for the effect of the $Si_{1-x}Ge_x$ interlayer is rather sketchy at this moment, it nevertheless describes the principal effect of the interlayer which gives rise to the suppression of C condensation and phase separation.

In summary, we have examined $Si_{1-x-y}Ge_xC_y$ film evolution on Si(001) clean surfaces by STM. The atomic scale phase separation between Si–C and Si–Ge in the films with large C fractions was clearly identified by the simultaneous onset of 3D island formation and the presence of a $c(4\times4)$ reconstruction. The formation of a $Si_{1-x}Ge_x$ interlayer on the Si surface drastically changes the morphology of the subsequently grown $Si_{1-x-y}Ge_xC_y$ films, leading to a planar morphology of the film even for large C fractions.

[1] R. Duschl, O. G. Schmidt, and K. Eberl, *Properties of Silicon Germanium and SiGe:Carbon*, edited by E. Kasper and K. Lyutovich (INSPEC, IEE, London, 2000), p. 158, and references therein.

[2] O. G. Schmidt and K. Eberl, Phys. Rev. Lett. **80**, 3396 (1998).

[3] B. L. Stein, E. T. Yu, E. T. Croke, A. T. Hunter, T. Laursen, A. E. Bair, J. W. Mayer, and C. C. Ahn, Appl. Phys. Lett. **70**, 3413 (1997).

[4] H. J. Osten, J. Appl. Phys. **84**, 2716 (1998).

[5] H. J. Osten and P. Gaworzewski, J. Appl. Phys. **82**, 4977 (1997).

[6] Landoldt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, New Series, Group III, Vol. 17a, edited by O. Madelung (Springer, Berlin, 1982).

[7] H. Rücker, M. Methfessel, E. Bugiel, and H. J. Osten, Phys. Rev. Lett. **72**, 3578 (1994).

[8] N. Herbots, P. Ye, H. Jacobson, J. Xiang, S. Hearne, and N. Cave, Appl. Phys. Lett. **68**, 782 (1996); B.-K. Yang, M. Krishnamurthy, and W. H. Weber, J. Appl. Phys. **84**, 2011 (1998).

[9] H. Jacobsson, J. Xiang, N. Herbots, S. Whaley, P. Ye, and S. Hearne, J. Appl. Phys. **81**, 3081 (1997).

[10] J. Tersoff, Phys. Rev. B **45**, 8833 (1992).

[11] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[12] F. Wu and M. G. Lagally, Phys. Rev. Lett. **75**, 2534 (1995).

[13] K. M. Chen, D. E. Jesson, S. J. Pennycook, M. Mostoller, T. Kaplan, T. Thundat, and R. J. Warmack, Phys. Rev. Lett. **75**, 1582 (1995).

[14] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1998).

[15] For example, H. Nöreberg and G. A. D. Briggs, Surf. Sci. **430**, 154 (1999); O. Leifeld, D. Grützma-cher, B. Müller, K. Kern, E. Kaxiras, and P. C. Kelires, Phys. Rev. Lett. **82**, 972 (1999).

[16] O. G. Schmidt, C. Lange, K. Eberl, O. Kienzle, and F. Ernst, Appl. Phys. Lett. **71**, 2340 (1997).

[17] R. W. Olesinki and G. J. Abbaschian, Bull. Alloy Phase Diagrams **5**, 484 (1984).

[18] P. C. Kelires, Phys. Rev. Lett. **75**, 1114 (1995).

[19] L. Patthey, E. L. Bullock, T. Abukawa, S. Kono, and L. S. O. Johansson, Phys. Rev. Lett. **75**, 2538 (1995).

[20] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1989), p. 11.

Downloaded 18 Oct 2006 to 133.6.32.11. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp