# Sn submonolayer-mediated Ge heteroepitaxy on Si(001)

X. W. Lin, Z. Liliental-Weber, J. Washburn, and E. R. Weber
*Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

A. Sasaki, A. Wakahara, and T. Hasegawa
*Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan*
(Received 29 September 1994)

The influence of a Sn submonolayer on the growth mode of Ge on Si(001) during molecular-beam epitaxy has been studied by transmission-electron microscopy and reflection high-energy electron diffraction. It was found that Sn-mediated growth promotes Ge island formation, suggesting that Sn acts to enhance the surface mobility of Ge adatoms. It is pointed out that being able to uniformly cover and strongly segregate to the growing surface is necessary, but not sufficient, for a surfactant to effectively suppress Ge islanding on Si.

## I. INTRODUCTION

Heteroepitaxy of Ge on Si is typical of the Stranski-Krastanov (SK) growth mode, i.e., Ge first grows layer by layer in a two-dimensional (2D) fashion, until it reaches a critical thickness $d_{SK}$, beyond which Ge islands begin to nucleate and the layer grows three dimensionally (3D).[1-3] For Ge growth on Si(001), $d_{SK}$ ranging from 3 to 6 monolayers (ML) has been reported.[1,2,4-6] The formation of Ge islands is highly undesirable for potential applications in electronics and optoelectronics of Ge/Si-based quantum-well structures (or superlattices), because it facilitates structural defect formation and degrades the interface quality. In the search for ways to overcome this problem, it has been found that the growth mode of Ge can be drastically altered by passivating the Si surface with a layer of surface-active species, called surfactants, prior to Ge growth by molecular-beam epitaxy (MBE).[7] Arsenic was the first discovered surfactant that is capable of suppressing Ge islanding and forcing Ge to grow in 2D far beyond $d_{SK}$.[5,8,9] Later, many other elements, including Sb,[9-12] Te,[12-14] Ga,[15] and Bi,[16,17] were found to act like As, as well. Two conditions seem to be necessary in order for a surfactant to suppress the island formation. First, it must strongly segregate to the growing surface and keep virtually floating on top of it. Second, the surfactant, normally $\leq 1$ ML thick, must wet (i.e., uniformly cover) the growing surface. Both these two conditions are satisfied for growth mediated by the above surfactant species. The same is also true for surfactant-mediated Si homoepitaxy.[18-20] However, these two conditions, albeit necessary, are not sufficient for the suppression of island formation.

In fact, recent studies of Sn-mediated Ge/Si heteroepitaxy[21-23] or Si homoepitaxy[24,25] demonstrated that Sn acts in the opposite manner, as compared with the above surfactants. Similar results were also found for Pb-mediated growth,[26] though both Sn and Pb proved to be strong surface segregants and wet Ge and Si surfaces, satisfying the above two surfactant conditions. If Sn and Pb are also to be called surfactants, they are clearly very different from those represented by As.

Tin surface segregation and the effects of Sn on Si and Ge epitaxy have previously been studied by a variety of techniques, including reflection high-energy electron diffraction (RHEED), Auger electron spectroscopy, x-ray diffraction, and Raman spectroscopy.[21-23] Ge/Si superlattices grown with Sn surfactant have also been characterized. The research on Sn surfactant not only provides insight into the mechanism of surfactant-mediated epitaxy, but also has its own merit, in the sense that Sn belongs to the same group of elements as Si and Ge, and thus does not behave as a dopant when incorporated into the matrix of an epilayer. In contrast, most of the other surfactants are shallow-level dopants and can result in an undesirable level of doping background ($10^{18}$–$10^{19}$ $cm^{-3}$), when gradually incorporated into the growing material.[7] Although all the surfactants are strong surface segregants, there still exists a small rate of incorporation that suffices to cause them to be buried in the epilayer and spread over a finite thickness.

In this study, transmission electron microscopy (TEM) was used in combination with RHEED to investigate the influence of 0.5 ML Sn on the MBE growth of Ge on Si(001) and the resulting morphology of Ge epilayers. Ge growth with other submonolayer Sn coverages was also examined. It will be demonstrated that Sn-mediated epitaxy promotes Ge islanding, characterized by a reduction in $d_{SK}$ and an increase in surface roughness, as compared with direct Ge growth on clean Si. The results will be discussed in terms of Sn-induced enhancement in adatom surface mobility, as well as in relation to our general understanding of the mechanism of surfactant-mediated epitaxy.

## II. EXPERIMENTAL DETAILS

All samples were prepared in a MBE chamber [base pressure $\approx(2.5-6.0)\times10^{-11}$ Torr], using $n$-type Si(001) wafers (10 $\Omega$ cm) as the substrate. An atomically clean Si

surface was obtained by chemical etching, followed by heating at 900 °C for 10 min in the MBE chamber. Following the growth of a 50-nm-thick Si buffer layer at 620 °C, the substrate temperature was lowered to 450–500 °C and a Sn layer of 0.5 ML coverage was deposited on the Si surface, prior to the growth of Ge epilayers up to a nominal thickness of 10 ML. (1 ML $=6.8\times10^{14}$ atoms cm$^{-2}$ for both Sn and Ge.) RHEED observations indicated that the Si surface prior to Sn deposition exhibited a $2\times1$ double-domain reconstruction. The growth rate of Ge was $\approx0.3$ ML s$^{-1}$, as calibrated using RHEED intensity oscillations. The Sn coverage on Si(001) was determined based on surface reconstructions[22,27,28] on Si(001). It was found that one period of RHEED intensity oscillations from Sn growth on Si(001) corresponded to a 0.5 ML coverage.

The Ge growth mode with or without Sn was monitored *in situ* by a RHEED system, operated at an accelerating voltage of 18 kV. Samples with various Ge thicknesses were examined *ex situ* by TEM, employing a JEOL 200CX high-resolution electron microscope. Prior to removal from the MBE chamber, the Ge surface was protected by depositing a Si capping layer $\approx10$ nm thick at room temperature at a deposition rate of $\approx0.3$ ML s$^{-1}$. Both plan-view and cross-sectional TEM specimens were prepared by mechanical grinding, followed by ion milling on a liquid-nitrogen-cooled stage.

Besides the 0.5 ML samples, effects of other submonolayer Sn coverages (0.12–1 ML) were also studied. In the following, however, we will mainly report the results of samples grown with and without a 0.5 ML Sn coverage.

## III. RESULTS

Figure 1 displays two sets of RHEED patterns, comparing the evolution of Ge growth mode with and without 0.5 ML Sn at $\approx460$ °C. In principle, a streaky RHEED pattern corresponds to reflections from a 2D layer, while a spotty pattern results from the formation of a 3D layer. The transition from a streaky to a spotty pattern is directly related to the onset of Ge islanding, and the corresponding Ge thickness has been defined above as the SK critical thickness $d_{SK}$. As shown in Fig. 1, while Ge growth without Sn [Fig. 1(a)] exhibits a 2D-3D transition at $d_{SK}\approx5$ ML, the presence of Sn [Fig. 1(b)] reduces $d_{SK}$ to $\approx4$ ML. In addition, the 2D-3D transition at $d_{SK}$ seems to occur more abruptly in the latter case, as compared with a progressive transition in the former. These observations suggest that the Sn-mediated epitaxy promotes Ge islanding, as opposed to other surfactants (As, Sb, etc.).[7–17]

The dependence of $d_{SK}$ on Sn coverage was also investigated. While no change in $d_{SK}$ was detected for a 0.12 ML Sn coverage, it was found that Sn coverage in the range 0.25–1 ML resulted in the same $d_{SK}$ reduction, i.e., to the value of $d_{SK}\approx4$ ML.[21,22]

In addition to the value of $d_{SK}$, the faceting behavior of Ge islands was also affected by Sn. RHEED patterns from the Sn-mediated growth [Fig. 1(b)] indicate {113}-type faceting, immediately after Ge island formation, whereas Ge islanding without Sn [Fig. 1(a)] displays a gradual change in facets from {118} at the initial stage of islanding to {113} for well-developed islands.

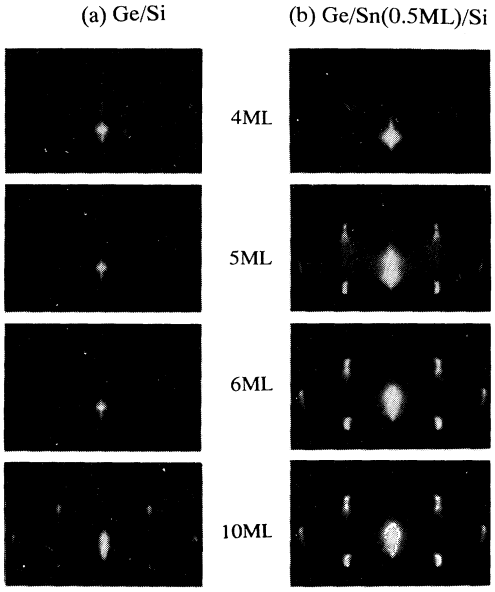


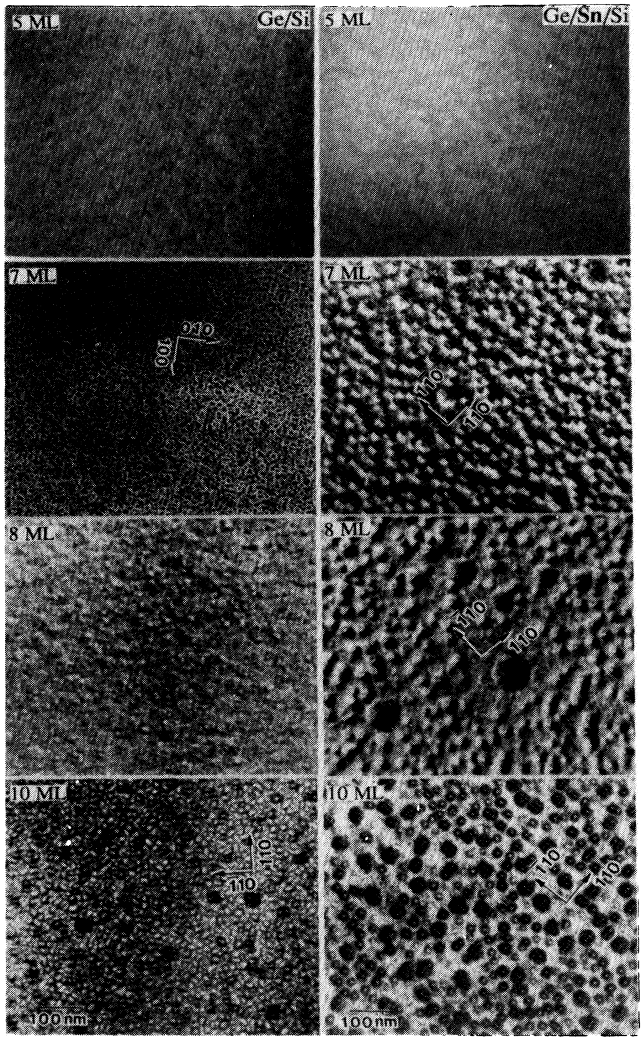

FIG. 1. RHEED patterns of Ge grown on Si(001) at $\approx460$ °C for thicknesses up to 10 ML (a) without and (b) with the presence of 0.5 ML Sn. The micrographs were recorded along the [110] azimuth. Note that Ge islanding occurs at 5 and $\approx6$ ML for growth with (b) and without (a) Sn, respectively.

Previous work has demonstrated that Sn tends to segregate to the growing surface of Ge during MBE.[21–23,29] This phenomenon can also be noticed by comparing the RHEED patterns for the 4 ML Ge growth with and without Sn. As shown in Fig. 1, direct growth of 4 ML Ge on Si(001) displays an eightfold surface reconstruction, while the Sn-mediated growth shows a sixfold reconstruction. The former is typical of direct Ge epitaxy on Si at low coverages (3–4 M),[30,31] corresponding to the previously reported $8\times2$ superstructure,[31] while the latter is the same as observed for direct deposition of 0.5 ML Sn on either a clean Si(001) or Ge(001) surface, and corresponds to a $6\times2$ superstructure.[22,27,28] Therefore, for the Ge(4 ML)/Sn/Si epitaxy, the first deposited 0.5 ML Sn must have segregated to the Ge surface, giving rise to the sixfold surface reconstruction.

The morphology of the Ge thin films was readily revealed by TEM. Figure 2 compares the plan-view images of two sets of samples grown at 500 °C with and without Sn, respectively. For a 5 ML Ge deposition, images of uniform contrast were observed for samples grown both with and without Sn. Thus the Ge layer in both cases grew essentially in 2D and was fully coherent (pseudomorphic) to the Si substrate. When its thickness exceeded $d_{SK}$, the Ge layer began to grow in 3D, with the surface morphology strongly depending on whether a 0.5 ML Sn layer was first deposited. Note that there seems to be some discrepancy in $d_{SK}$ between the values estimated from RHEED and TEM. For the Ge/Sn/Si epi-

taxy, in particular, Fig. 1(b) suggests $d_{SK} \approx 4$ ML, while Fig. 2(b) shows no sign of Ge islands at 5 ML. This apparent discrepancy may be attributed to the difference in sensitivity of the above two techniques in detecting the surface roughness.

In the absence of Sn, Ge growth to 7 ML resulted in a mottled structure, characterized by a network of interconnected white segments $\approx 3$ nm wide and $\approx 15$ nm long [Fig. 2(a)]. All the segments are practically aligned along either of the two orthogonal $\langle 100 \rangle$ directions in the surface plane. They correspond to the previously reported faceted Ge islands (hut clusters),[6,32] and give rise to surface roughness of the Ge layer. With increasing Ge thickness, the degree of surface roughness increased, accompanied by considerable changes in surface morphology. It can be seen in Fig. 2(a) that the 8 ML Ge sample exhibits a granular contrast, while the 10 ML sample displays a mosaic structure. The latter consists predominantly of Ge islands $\approx 20$ nm in diameter, in addition to some larger ones ($\approx 40$ nm in diameter) associated with a network of orthogonal moiré fringes running along [110] and [$\bar{1}$10]. Interestingly, the whole sample surface is covered by Ge islands, whose peripheries are in close contact to one another, leaving virtually no flat areas in between them. Conventional diffraction-contrast analysis[33] indicated that the small islands are coherent to the Si substrate, while the larger ones are strain relaxed due to the formation of perfect-edge misfit dislocations (Burgers vectors $\mathbf{b} = \frac{1}{2}a\langle 110 \rangle$) running along $\langle \bar{1}10 \rangle$. The same result can also be deduced from cross-sectional TEM observations (Fig. 3). Furthermore, Fig. 3 shows that both types of Ge islands are of rounded shape, and that for the large, dislocated ones the aspect ratio (height to base diameter) is $\approx 1{:}6$.




(a) (b)

FIG. 2. Plan-view TEM micrographs of Ge grown on Si(001) at 500 °C for thicknesses up to 10 ML (a) without and (b) with the presence of 0.5 ML Sn. Note that islands associated with a network of orthogonal moiré fringes along [110] and [$\bar{1}$10] are strain relaxed, with the formation of perfect-edge misfit dislocations, whereas islands with black/white contrast are fully coherent to the Si substrate. Ge hut clusters, aligned in either [100] or [010], can be seen in (a) for 7 ML Ge.

In the presence of Sn, Ge islanding results in a quite different surface morphology from that without Sn. Several features can be noticed in Fig. 2(b) for 7–10 ML Ge depositions. First, Sn-mediated growth results in a rougher surface than direct Ge epitaxy on Si, as evidenced by comparing the 7 or 8 ML samples with and without Sn. This is consistent with the above RHEED observation, in that Sn atoms tend to promote 3D growth.

Second, all Ge islands are well separated from one another by relatively flat surface areas in between them. Each island appears as a spherical cap in shape, with a circular base and a rounded cross section, as confirmed by cross-sectional TEM (Fig. 4). This feature is in direct contrast to that observed for samples grown without Sn—see, for instance, the 10 ML Ge/Si sample in Fig. 2(a).

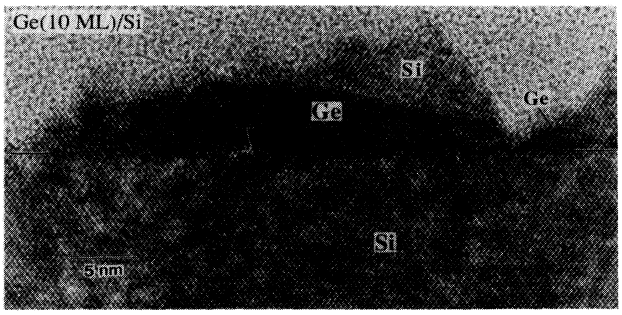



FIG. 3. Cross-sectional high-resolution TEM micrograph of a 10 ML Ge sample grown without Sn on Si(001)—the same as shown in Fig. 2(a). Note the formation of a large dislocated Ge island and a small coherent island, whose peripheries are in close contact with each other. The arrow indicates a perfect-edge misfit dislocation at the Ge/Si interface.

Third, the Ge islands display a bimodal size distribution, representing two groups of islands: The small islands (diameter $\approx 18$ nm) are coherent with respect to the Si substrate, while the large ones (diameter $> \approx 25$ nm), characterized by a network of orthogonal moiré fringes along [110] and [$\bar{1}$10], are strain relaxed, with the formation of perfect-edge misfit dislocations.

Finally, the relative number of coherent versus dislocated islands varies gradually with Ge thickness. For 7 ML Ge, the number of coherent islands ($\approx 6\times 10^{10}$ $cm^{-2}$) is predominant, about 40 times greater than that of dislocated islands ($\approx 1.5\times 10^{9}$ $cm^{-2}$). Increasing Ge thickness results in a decrease in the number of coherent islands, accompanied by an increase in the number of dislocated islands. These two numbers become comparable, for a 10 ML Ge deposition. The evolution of island coherency and size distribution is interesting on its own, but will be further treated in a separate publication. It will not be discussed below, in order to focus the discussion on the effects of the Sn surfactant.

Figure 4 shows the cross sections of a coherent and a dislocated Ge island, typically found in a Ge (10 ML)/Sn/Si sample. Despite the large difference in size, both islands exhibit a similar aspect ratio of $\approx 1{:}3$, which is twice that measured for islands grown without Sn (Fig. 3). A higher island aspect ratio for Ge/Sn/Si implies a rougher surface than that of Ge/Si samples, consistent with the above plan-view observations (Fig. 2). For the dislocated island [Fig. 4(a)], a perfect-edge misfit dislocation is readily recognized in the middle of the Ge/Si interface. Furthermore, it can be seen that the Ge{111} planes near the island edges rotate slightly with respect to those in the middle of the island, where the Ge lattice is practically strain relaxed. This is expected, because the strain induced by the lattice mismatch between an island and a substrate is strongest near the island edges.[34] As for the coherent island [Fig. 4(b)], the Ge lattice is elastically strained to perfectly match the Si substrate. Outside the island, a uniform Ge layer $\approx 6$ ML thick can be seen between the Si substrate and the cap. It is the Ge wetting layer, characteristic of SK growth. Note that one bright dot in the high-resolution images in Figs. 3 and 4 corresponds to 2 ML ($\approx 0.28$ nm for unstrained Ge) along [001].

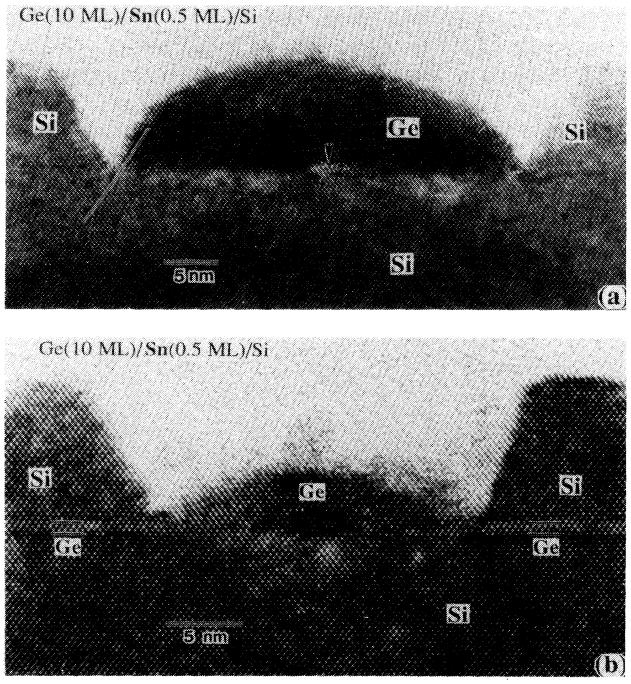



FIG. 4. Cross-sectional high-resolution TEM micrographs of a 10 ML Ge sample grown with Sn on Si(001)—the same as shown in Fig. 2(b). (a) A large, dislocated Ge island, with the formation of a perfect-edge misfit dislocation at the Ge/Si interface (marked by arrow). Lattice tilting can be seen at the edges of the Ge island. (b) A small, coherent Ge island on Si. A Ge wetting layer between the Si substrate and cap is seen to continue beyond the two edges of the island.

In Fig. 4(b), it can be noticed that the Si cap, grown at room temperature, is epitaxial on the Ge wetting layer, but becomes amorphous, after a limited epitaxial growth above the coherent Ge island. This observation suggests that the low-temperature growth mode of a Si overlayer is influenced by its lattice mismatch with the substrate. Since the Ge wetting layer is fully strained (i.e., pseudomorphic) to the underlying Si substrate, the Si cap grows on a lattice-matched Ge substrate and involves no strain energy. Consequently, the Si cap is expected to grow epitaxially to an extended thickness. On the other hand, the coherent Ge island is relatively strain relaxed, resulting in a Si/Ge lattice mismatch that varies progressively along the island free surface. Due to this lattice mismatch, Si growth on top of the Ge island involves extra strain energy, which causes Si to grow in amorphous phase, following a limited epitaxy. Similar observation can also be made in Fig. 3 for Ge islands grown without Sn. As for the dislocated Ge island shown in Fig. 4(a), the relatively large island height allows for more strain relaxation at the island surface and thus results in a greater Si/Ge lattice mismatch, as compared with the islands shown in Figs. 3 and 4(b). As a consequence, the Si cap grows almost immediately in amorphous phase. This result suggests that increasing the lattice mismatch promotes the growth of amorphous phase. Note that if the Si cap were grown at elevated temperatures (e.g., 500 °C), relevant thermal processes would be sufficiently activated to allow unlimited epitaxial growth, probably with the formation of some defects (e.g., misfit dislocations or stacking faults), depending on the actual lattice mismatch between the Si cap and the underlying Ge island.

## IV. DISCUSSION

We have demonstrated that Sn-mediated Ge growth on Si promotes islanding, as evidenced by the reduction of $d_{SK}$ and the formation of a rougher surface, compared with direct Ge epitaxy on Si. This is in direct contrast with the growth mediated by other surfactants (e.g., As and Sb), in which Ge islanding is suppressed and the Ge epilayer grows in 2D far beyond $d_{SK}$ measured for direct

heteroepitaxy.[7-17] In order to understand the effects of Sn, let us first consider the mechanism of Ge island formation on a clean Si surface.

For a SK system such as Ge on Si(001), it is generally believed that the fundamental driving force for island formation is the reduction of strain energy induced by lattice mismatch.[35,36] During the initial growth stage, the epilayer grows in 2D, with a strain energy that increases with increasing thickness, until the onset of islanding for thickness $>d_{SK}$. Prior to the introduction of misfit dislocations, 3D coherent islands are the first ones to form. They not only allow for an effective lateral relaxation of the film, but also result in a graded elastic strain field in the substrate, which further contributes to the total strain relaxation of the system.[37,38] The equilibrium surface morphology of the system is determined by the balance between the energy reduction due to strain relaxation and the increase in surface energy caused by 3D growth.[35] Generally, the rougher the surface morphology of an epilayer, the more effective will be the lateral strain relaxation. In other words, the system prefers the formation of 3D islands with large aspect ratios. At later stages of island growth, the coherency of Ge islands cannot be maintained, and the formation of misfit dislocations at the Ge/Si interface becomes the dominant mechanism for strain relaxation.

In order for the system to reach the equilibrium state, adatoms on the surface must be sufficiently mobile to form well-developed islands. The growth of a system may be kinetically limited and the surface roughness can depend on the growth conditions. The underlying kinetic parameter is the surface diffusion length $L$, which is related to surface diffusion coefficient $D_s$ and deposition rate $R$ (ML s$^{-1}$) by the equation $L=\sqrt{D_s/R}$. Since one generally can write $D_s \propto \exp(-E/kT)$, where $E$ is the hopping activation energy and $T$ the growth temperature, the surface diffusion length not only depends on $R$, but also depends exponentially on $E$ and $T$. Any significant change in these three parameters will lead to a variation in $L$ and, thereby, modification of surface morphology. The larger the value of $L$, the closer the system will be to the equilibrium state and hence the greater will be the surface roughness. Conversely, if a small value of $L$ is maintained during growth, island formation will be hindered and the system tends to grow in 2D. There exists extensive experimental and computer-simulation evidence in support of this kinetic model for surface roughening (islanding) of heteroepitaxy.[36] In the case of Ge epitaxy on Si, it has previously been shown that lowering the growth temperature promotes 2D growth.[39,40] The use of such surfactants as As and Sb also promotes layer-by-layer growth beyond $d_{SK}$, because they effectively reduce surface diffusion by promoting subsurface incorporation of Ge adatoms via an atomic-site exchange mechanism,[41-43] which is equivalent to increasing the value of $E$ (Ref. 44). Interestingly, although the passivation by a surfactant may lower the surface energy of the growth front and thus energetically affect the growth mode, it is the kinetics that actually controls the epitaxial behavior of Ge and Si under normal growth conditions.

For Sn-mediated growth over $d_{SK}$, we observed a rougher Ge surface morphology than for growth without Sn. According to the above kinetic model for surface roughening, we conclude that the 0.5 ML Sn plays the role of *enhancing* the surface mobility of Ge adatoms, which is contrary to As or other surfactants (except Pb), though all of them are similar in terms of surface segregation and surface wettability. This conclusion is further supported by the following observations.

(1) Ge islands grown with Sn not only display a greater aspect ratio (rougher surface), but also appear to be well separated from one another by flat surface areas (the Ge wetting layer) [Fig. 2(b)], as compared with those grown without Sn [see the 10 ML sample in Fig. 2(a)]. This separation of individual islands requires considerable surface mobility (i.e., large $L$) that allows Ge adatoms deposited on the flat regions to quickly move to an island and most effectively contribute to 3D growth and strain minimization. On the other hand, a relatively small value of $L$ impedes the development of a 3D island, and causes an increase in the island nucleation rate in the flat surface regions. As a result, islands with a relatively small aspect ratio and a small interisland spacing are expected. The latter may bring islands into close contact with one another and leaves virtually no flat surface area in between them.

(2) The presence of Sn leads to reduction of $d_{SK}$. Under normal growth conditions, direct growth of Ge on Si may be kinetically limited, especially because the growth rate (0.3 ML s$^{-1}$) used in this work is considerably greater than that ($\approx 10^{-2}$ ML s$^{-1}$) used in most previous studies. As a result, the measured $d_{SK}$ value may exceed the one that would correspond to equilibrium growth conditions. Any increase in adatom mobility (i.e., $L$) is expected to bring $d_{SK}$ closer to the true equilibrium value. This is certainly the case for Sn-mediated growth, in which the increase in $L$ induced by Sn results in the reduction of $d_{SK}$.

Furthermore, our conclusion of Sn-induced enhancement in surface mobility is consistent with previously reported results. First, comparative studies of Sn- and Sb-mediated growth of Si/Ge superlattices on Ge(001), instead of Si(001), demonstrated that submonolayer coverage of Sn prior to Si/Ge epitaxy causes island formation and destroys the sharpness of Si/Ge interfaces, as opposed to Sb which improves the structural quality.[23] This result can be accounted for by assuming that Sn enhances the mobility of Si and promotes Si islanding on Ge; Si growth on Ge is of Volmer-Weber mode (growth with immediate islanding).[3]

Second, in contrast to growth on Ge(001), if a Ge/Si superlattice is grown on Si(001) with each Ge epilayer $\leq 3$ ML thick, the use of Sn was found to improve the interface quality.[21] Since the thickness of each Ge layer never exceeded $d_{SK}$, the 2D growth mode is expected to be maintained, either with or without Sn. However, due to increased surface mobility, Sn has the effect of smoothing the growing Ge surface, by allowing adatoms to be quickly incorporated at surface steps and thus reducing 2D island nucleation. As a result, a flatter Si/Ge interface is expected, compared with growth without Sn. For

comparison, since surfactants such as As and Sb reduce the surface mobility, they actually degrade the interface flatness for 2D growth, by increasing the surface step density.[16,17] In addition to the interface flatness, the interface abruptness can also be improved by the use of Sn, because Sn is a strong surface segregant and can act as other surfactants[16,17,45–47] to drastically reduce the likelihood of Ge segregation during Si overgrowth on Ge.

Third, the smoothing effect of Sn has been clearly demonstrated in a study of Sn-mediated Si(111) homoepitaxy.[24,25] It was shown that the transition temperature from 2D-island nucleation to step-flow growth mode can be substantially lowered by the presence of Sn atoms. This result can be understood in terms of Sn-induced enhancement in adatom mobility.

At present, the mechanism by which the surface diffusion is enhanced by Sn atoms is unclear. Nevertheless, one can gain some insight into this mechanism by comparing Sn with other surfactants (As, Sb, Pb, etc.) and pointing out the distinct features of Sn-mediated epitaxy. To simplify the following discussion, we shall mention As to represent all elements (As, Sb, etc.) that are capable of suppressing Ge islanding on Si.

(1) Although both Sn and As strongly segregate to the growing surface of Ge or Si, they display opposite effects on the growth mode of Ge on Si. Surface segregation necessarily involves site exchange between adatoms and the underlying surface atoms. Once an adatom is incorporated in the subsurface, its mobility is greatly reduced. For As-mediated growth, the site exchange between As and Ge occurs primarily on surface terraces, shortly after impingement of incoming Ge atoms on the surface.[41–43] This segregation process is believed to be responsible for the suppression of Ge island formation. Had the same process occurred for Sn-mediated epitaxy, one would have observed the absence of Ge islanding, as well. The fact that Sn promotes 3D Ge growth suggests that Sn atoms must segregate in a different fashion as compared with As atoms.

(2) Among the previously studied surfactants, Pb (Refs. 26, 48, and 49) shows great similarity to Sn (Refs. 21–23) in many aspects, such as the surface segregation, the influence on Ge islanding on Si, the chemisorption site, the surface reconstruction, and the growth mode on Si(001) (both are of the SK mode), despite their difference in atomic size. This does not seem surprising, considering the fact that both Sn and Pb are group-IV elements, the same as Si and Ge, and possess the same nominal chemical valence. In contrast, surfactants like As, Sb, and Te belong to other groups of elements and behave oppositely to Sn and Pb during Ge/Si heteroepitaxy. Obviously, there exist two types of surfactants: Type I includes As, Sb, Bi, Te, and Ga, and type II corresponds to Sn and Pb. The fact that the type-II elements share the same nominal electronegativity with the epitaxial materials (Si and Ge) certainly gives rise to distinct atomic interactions on the growing surface. Properties such as the Sn-Si bond strength and the position of Sn monomers or dimers with respect to the Si surface may be qualitatively different from those for the As-Si interaction. For instance, Sn adatoms on Si(111) prefer the $T_4$ site, whereas As occupies the substitutional site.[50] As a result, different behaviors in surfactant surface segregation and different effects on Ge adatom diffusion are expected.

The above two types (I and II) of surfactants have previously been discussed by Massies and Grandjean, and referred to as reactive and nonreactive surfactants, respectively.[51] These denominations are reasonable ones, since the reactivity of an element with Si or Ge is directly related to its electronegativity. In addition, it was proposed that the type-I atoms occupy substitutional sites on the Si or Ge surface (i.e., are on the sites that would be taken by Si or Ge adatoms on a clean surface), as opposed to the type-II atoms which reside on interstitial surface sites. While the former is definitely true, based on extensive experimental and theoretical studies,[41–43] convincing evidence for the latter is still lacking. In fact, the actual situation is much more complex, because of such factors as the Sn-Sn, Sn-Si, or Sn-Ge interactions (i.e., dimerization) and the overall surface reconstruction.[28]

In order to develop an atomistic model for the Sn-mediated epitaxy, one needs to systematically study the interaction between Sn and Ge (or Si) adatoms and its consequences on surface diffusivity. The techniques (TEM and RHEED) used in this work are unfortunately inadequate to provide any direct evidence on surface diffusion mechanisms. Other methods, such as scanning tunneling microscopy and low-energy electron microscopy, appear more promising and should be used in future studies.

## V. CONCLUSIONS

The effects of a Sn submonolayer (up to 1 ML) on the heteroepitaxy of Ge (up to 10 ML) on Si(001) were studied by TEM and RHEED. The results presented above were mainly concerned with comparison of the samples grown with and without a 0.5 ML Sn coverage.

(1) Growth in the presence of Sn results in a reduction in $d_{SK}$ and an increase in surface roughness of Ge epilayers, as compared with direct Ge growth on Si. The Sn-mediated epitaxy promotes Ge island formation.

(2) It was suggested that Sn enhances the surface diffusion length of adatoms during Ge/Si heteroepitaxy.

(3) Comparative analysis of Sn and other surfactants indicates that there exist two types of surfactants, exhibiting opposite effects on homoepitaxy or heteroepitaxy of Ge and Si: While type II corresponds to Sn and Pb, belonging to the same group of elements as Ge and Si (group IV), type I includes As, Sb, Te, etc., belonging to other groups of elements.

(4) This work points out that being able to uniformly cover and strongly segregate to the growing surface is necessary, but not sufficient, for a surfactant to be efficient in suppressing Ge island formation on Si. Further studies are required to elucidate the microscopic mechanism of Sn-mediated epitaxy.

## ACKNOWLEDGMENTS

This work was supported by the SDIO/IST program, administrated through ONR under Contract No.

N00014-86-K-0668. The use of the facilities of the National Center for Electron Microscopy was supported by the Director, Office of Energy Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The work done in Japan was also supported by Grant-in-Aid No. 4227107 from the Ministry of Education, Science and Culture of Japan. We wish to thank W. Swider for TEM sample preparation.

[1]M. Asai, H. Ueba, and C. Tatsuyama, J. Appl. Phys. **58**, 2577 (1985).
[2]J. Bevk, J. P. Mannaets, L. C. Feldman, B. A. Davidson, and A. Ourmazd, Appl. Phys. Lett. **49**, 286 (1986).
[3]P. M. J. Marée, K. Nakagawa, F. M. Mulders, J. F. van der Veen, and K. L. Kavanagh, Surf. Sci. **191**, 305 (1987).
[4]K. Miki, K. Sakamoto, and T. Sakamoto, in *Chemistry and Defects in Semiconductor Heterostructures,* edited by M. Kawabe, T. D. Sands, E. R. Weber, and R. S. Williams, MRS Symposia Proceedings No. 148 (Materials Research Society, Pittsburgh, 1989), p. 323.
[5]M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[6]Y. W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).
[7]For a review on this subject, see, e.g., E. Tournié and K. H. Ploog, Thin Solid Films **231**, 43 (1993).
[8]F. K. LeGoues, M. Copel, and R. Tromp, Phys. Rev. Lett. **63**, 1826 (1989).
[9]M. Copel, M. C. Reuter, M. Horn von Hoegen, and R. M. Tromp, Phys. Rev. B **42**, 11 682 (1990).
[10]J. M. C. Thornton, A. A. Williams, J. E. Macdonald, R. G. van Silfhout, J. F. van der Veen, M. Finney, and C. Norris, J. Vac. Sci. Technol. B **9**, 2146 (1991).
[11]H. J. Osten, G. Lippert, and J. Klatt, J. Vac. Sci. Technol. B **10**, 1151 (1992).
[12]H. J. Osten, J. Klatt, G. Lippert, E. Bugiel, and S. Higuchi, J. Appl. Phys. **74**, 2507 (1993).
[13]S. Higuchi and Y. Nakanishi, J. Appl. Phys. **71**, 4277 (1992).
[14]X. Yang, R. Cao, J. Li, J. Terry, J. Wu, and P. Pianetta, in *Common Themes and Mechanisms of Epitaxial Growth,* edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. F. Kuech, MRS Symposia Proceedings No. 312 (Materials Research Society, Pittsburgh, 1993), p. 243.
[15]J. Falta, M. Copel, F. K. Le Goues, and R. M. Tromp, Appl. Phys. Lett. **62**, 2962 (1993).
[16]K. Sakamoto, K. Kyoya, K. Miki, H. Matsuhata, and T. Sakamoto, Jpn. J. Appl. Phys. **32**, L204 (1993).
[17]K. Sakamoto, H. Matsuhata, K. Kyoya, K. Miki, and T. Sakamoto, Jpn. J. Appl. Phys. **33**, 2307 (1994).
[18]K. Sakamoto, K. Miki, T. Sakamoto, H. Matsuhata, and K. Kyoya, J. Cryst. Growth **127**, 392 (1993).
[19]B. Voigtländer and A. Zinner, Surf. Sci. Lett. **292**, L775 (1993).
[20]H. Nakahara and M. Ichikawa, Appl. Phys. Lett. **61**, 1531 (1992).
[21]K. K. Vong, A. Wakahara, and A. Sasaki, in *Proceedings of the 6th Topical Meeting on Crystal Growth Mechanism,* edited by T. Nishinaga (University of Tokyo, Tokyo, 1992), p. 295.
[22]A. Wakahara, K. K. Vong, T. Hasegawa, A. Fujihara, and A. Sasaki (unpublished).
[23]W. Dondl, G. Lütjering, W. Wegscheider, J. Wilhelm, R. Schorer, and G. Abstreiter, J. Cryst. Growth **127**, 440 (1993).
[24]S. Iwanari and K. Takayanagi, Jpn. J. Appl. Phys. **30**, L1978 (1991).
[25]S. Iwanari and K. Takayanagi, J. Cryst. Growth **119**, 229 (1992); **119**, 241 (1992).
[26]H. Hibino, N. Shimizu, K. Sumitomo, Y. Shinoda, T. Nishioka, and T. Ogino, J. Vac. Sci. Technol. A **12**, 23 (1994).
[27]K. Ueda, K. Kinoshita, and M. Mannami, Surf. Sci. **145**, 261 (1984).
[28]A. A. Baski, C. F. Quate, and J. Nogami, Phys. Rev. B **44**, 11 167 (1991).
[29]H. J. Gossmann and L. C. Feldman, Appl. Phys. Lett. **48**, 1141 (1986).
[30]T. Nakayama, Y. Tanishiro, and K. Takayanagi, Surf. Sci. **273**, 9 (1992).
[31]N. Ohshima, Y. Koide, S. Zaima, and Y. Yasuda, Appl. Surf. Sci. **48/49**, 69 (1991).
[32]A. Sakai and T. Tatsumi, Phys. Rev. Lett. **71**, 4007 (1993).
[33]P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals,* 2nd ed. (Krieger, Malabar, FL, 1977).
[34]S. Guha, A. Madhukar, and K. C. Rajkumar, Appl. Phys. Lett. **57**, 2110 (1990).
[35]B. G. Orr, D. Kessler, C. W. Snyder, and L. Sander, Europhys. Lett. **19**, 33 (1992).
[36]N. Grandjean and J. Massies, J. Cryst. Growth **134**, 51 (1993).
[37]D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).
[38]S. Christiansen, M. Albrecht, H. P. Strunk, and H. J. Maier, Appl. Phys. Lett. **64**, 3617 (1994).
[39]D. J. Eaglesham and M. Cerullo, Appl. Phys. Lett. **58**, 2276 (1991).
[40]M. Krishnamurthy, J. S. Drucker, and J. A. Venables, J. Appl. Phys. **69**, 6461 (1991).
[41]R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 954 (1992).
[42]B. D. Yu and A. Oshiyama, Phys. Rev. Lett. **72**, 3190 (1994).
[43]T. Ohno, Phys. Rev. Lett. **73**, 460 (1994).
[44]H. J. Osten, Appl. Phys. Lett. **64**, 2356 (1994).
[45]P. C. Zalm, G. F. A. van de Walle, D. J. Gravesteijn, and A. A. van Gorkum, Appl. Phys. Lett. **55**, 2520 (1989).
[46]K. Fujita, S. Fukatsu, H. Yaguchi, T. Igarashi, Y. Shiraki, and R. Ito, Jpn. J. Appl. Phys. **29**, L1981 (1990).
[47]S. Fukatsu, N. Usami, K. Fujita, H. Yaguchi, Y. Shiraki, and R. Ito, J. Cryst. Growth **127**, 401 (1993).
[48]J. S. Pedersen, R. Feidenhans'l, M. Nielsen, K. Kjaer, F. Grey, and R. L. Johnson, Surf. Sci. **189/190**, 1047 (1987).
[49]H. Itoh, H. Tanabe, D. Winau, A. K. Schmid, and T. Ichinokawa, J. Vac. Sci. Technol. B **12**, 2086 (1994).
[50]J. P. LaFemina, Surf. Sci. Rep. **16**, 133 (1992).
[51]J. Massies and N. Grandjean, Phys. Rev. B **48**, 8502 (1993).

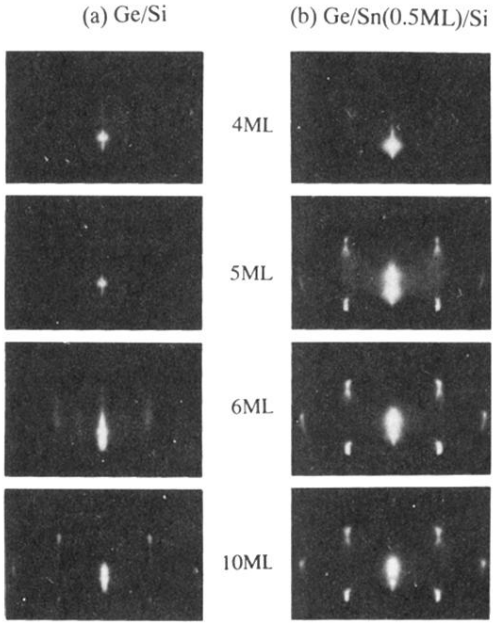
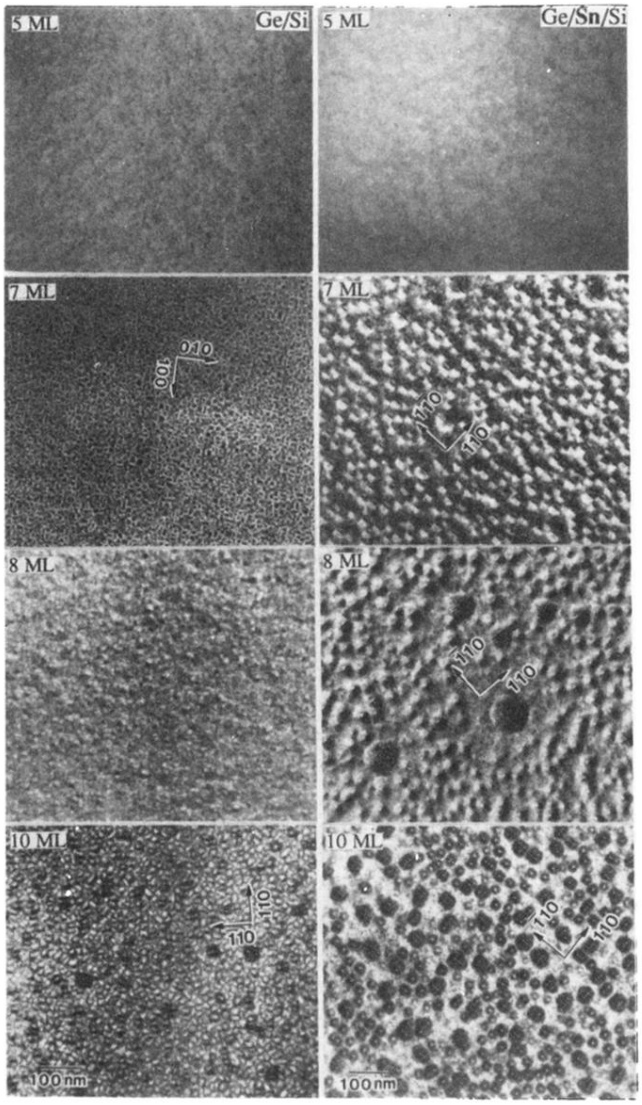



FIG. 1. RHEED patterns of Ge grown on Si(001) at $\approx 460\,^{\circ}\mathrm{C}$ for thicknesses up to 10 ML (a) without and (b) with the presence of 0.5 ML Sn. The micrographs were recorded along the [110] azimuth. Note that Ge islanding occurs at 5 and $\approx 6$ ML for growth with (b) and without (a) Sn, respectively.




(a) (b)

FIG. 2. Plan-view TEM micrographs of Ge grown on Si(001) at 500 °C for thicknesses up to 10 ML (a) without and (b) with the presence of 0.5 ML Sn. Note that islands associated with a network of orthogonal moiré fringes along [110] and [$\bar{1}$10] are strain relaxed, with the formation of perfect-edge misfit dislocations, whereas islands with black/white contrast are fully coherent to the Si substrate. Ge hut clusters, aligned in either [100] or [010], can be seen in (a) for 7 ML Ge.

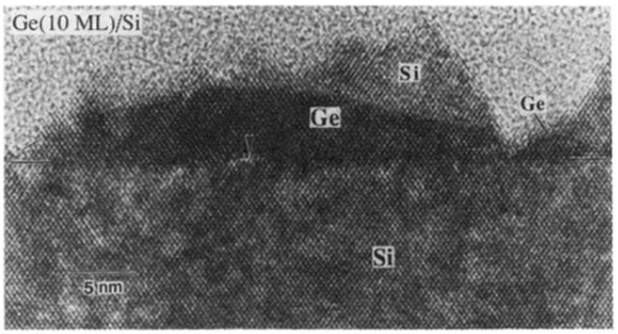



FIG. 3. Cross-sectional high-resolution TEM micrograph of a 10 ML Ge sample grown without Sn on Si(001)—the same as shown in Fig. 2(a). Note the formation of a large dislocated Ge island and a small coherent island, whose peripheries are in close contact with each other. The arrow indicates a perfect-edge misfit dislocation at the Ge/Si interface.

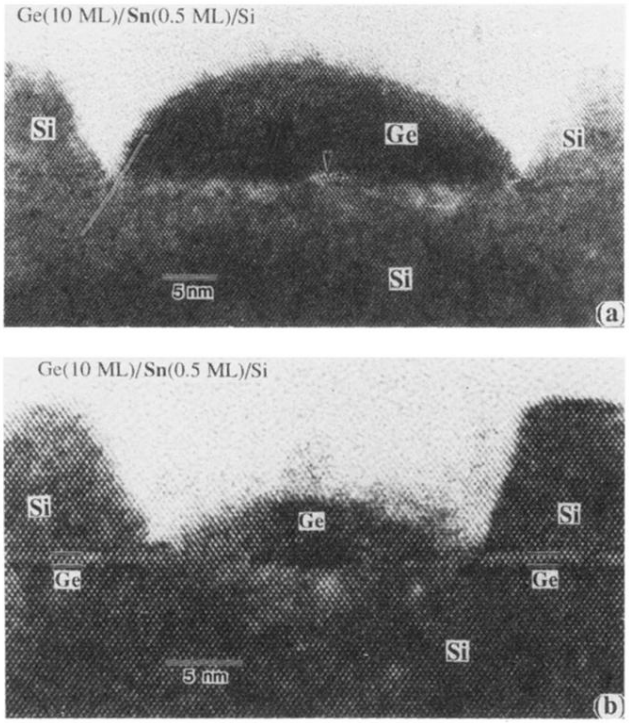



FIG. 4. Cross-sectional high-resolution TEM micrographs of a 10 ML Ge sample grown with Sn on Si(001)—the same as shown in Fig. 2(b). (a) A large, dislocated Ge island, with the formation of a perfect-edge misfit dislocation at the Ge/Si interface (marked by arrow). Lattice tilting can be seen at the edges of the Ge island. (b) A small, coherent Ge island on Si. A Ge wetting layer between the Si substrate and cap is seen to continue beyond the two edges of the island.