Surface-Stress-Induced Order in SiGe Alloy Films

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(Received 31 January 1990)

Ordering in epitaxial Si/Ge alloys grown by molecular-beam epitaxy has been observed by several authors. Attempts to explain this unusual phenomenon on the basis of the bulk thermodynamic properties of the alloy have failed. In this Letter we show that the observed ordering is not an equilibrium bulk property, but rather the result of surface growth kinetics. We attribute the ordering to atomic-scale stresses present in the reconstructed Si(001) surface during growth, leading to double-layer segregation of Ge and Si along one of the four equivalent ⟨111⟩ directions. This near-surface ordering is then quenched in as the crystal grows.

PACS numbers: 68.55.Bd, 68.35.Bs, 68.35.Md

Alloy ordering in single-crystal Si/Ge alloy films grown by molecular-beam epitaxy (MBE) has been observed by a number of authors.[1-4] In most studies the ordered alloy films were prepared so as to leave them stressed due to lattice mismatch, and the ordering has generally been attributed to this stress.[2,5]

However, LeGoues, Keson, and Iyer[1] have shown recently that the ordering occurs even in films which have no residual stress and that the actual ordering does not correspond to the structure of lowest energy. Thus, despite very extensive studies, there is at present no satisfactory explanation for this ordering.

Here we show that the ordering is not an equilibrium bulk phenomenon, but is tied specifically to the growth on the reconstructed Si(001) 2×1 surface. We propose a mechanism for the ordering, based on stress-induced local segregation at the surface. This explanation accounts for virtually all the experimental results to date, including the unexpected structure of the ordered phase.

Several theoretical[5-7] studies have tried to explain the ordering on the basis of the energetics and thermodynamics of the bulk Si/Ge alloy. While such studies have shown that ordering is favorable at low temperature, they also predict[8] a phase transition to a random alloy at temperatures in the range 60–100 K. Experimentally, the ordered alloy films are grown in the range 700–850 K, so no ordering is expected. Also, all such theoretical studies agree that the most stable ordered phase is the "microscopically unstrained" phase which corresponds to alternate SiGe and GeSi layers in the ⟨111⟩ directions. LeGoues, Kesan, and Iyer[1] have shown that this is not the structure observed experimentally. Instead, the structure is microscopically strained and corresponds to alternate SiSi and GeGe layers. Therefore, it appears that the ordering is not related to the low-temperature ordered phase predicted in the theoretical studies.

We have performed several experiments which directly demonstrate that the ordering is related to the surface structure and growth mode, rather than the bulk stress or equilibrium properties. The samples used were grown by solid-source MBE, between 390 and 625 °C on Si(001) and Si(111) substrates. The presence or absence of order was determined by planar-view and cross-sectional transmission electron microscopy. Surface reconstruction was determined by LEED.

A first set of samples, used to determine the role of substrate orientation and growth and annealing temperatures, consisted of a single layer of $Si_{0.5}Ge_{0.5}$. The thickness (7500 Å) was chosen to assure complete relief of the strain. Some of the samples were annealed to determine the temperature at which ordering disappears. Further anneals were performed to determine the reversibility of the order-disorder transition. Table I summarizes these results.

For samples grown on Si(001), strong order is observed at the lowest growth temperature (as had been demonstrated in Ref. 1). Order remains at 525 °C, but the intensity of the extra reflection has decreased, indicating a lower ordering parameter. Order has completely disappeared at 625 °C. The sample grown at 390 °C was annealed at various temperatures for 2 h. Order remains detectable up to a temperature of about 700 °C. Contrary to the report of Ourmazd and Bean,[2] once order is destroyed, further annealing is unable to restore it. Thus the ordered phase is metastable, and is not the equilibrium state of the alloy.

The layer grown on Si(111) did not show ordering, even at the lowest growth temperature. Thus it appears that the ordering is related to the surface orientation. To test that it is not only the surface orientation which matters, but the actual 2×1 dimer structure of the (001) surface, we grew films on a Si(001) sample that did not exhibit the 2×1 reconstruction. This was accomplished by saturating the Si(001) surface with about one monolayer of Sb.[9] The first 5000 Å of the sample were grown on the bare Si(001) substrate. LEED indicated that, as expected, this surface exhibited a 2×1 reconstruction. Then the surface was saturated with Sb. LEED showed that a 1×1 structure had replaced the 2×1 reconstruc-

TABLE I. Growth and annealing conditions and corresponding strength of the reflections due to ordering.

Substrate orientation	Growth temperature (°C)	Annealing conditions	Observed intensity of the ordering reflections
Si(001)	625	No anneal	No order
	525	No anneal	Medium-weak
	390	No anneal	Strong
		2 h, 450 °C	Strong
		2 h, 500 °C	Strong
		2 h, 550 °C	Medium
		2 h, 600 °C	Medium-weak
		2 h, 650 °C	Weak
		2 h, 700 °C	No order
		2 h, 800 °C + 6 h, 600 °C	No order
		2 h, 800 °C + 6 h, 500 °C	No order
		2 h, 800 °C + 6 h, 450 °C	No order
Si(111)	390	No anneal	No order

tion (see Fig. 1). Growth was continued for 5000 Å with a sustaining flux of Sb to compensate for the loss of Sb due to incorporation in the thin film. Our calibrations indicate that, at the overpressure of Sb used during the growth, a doping corresponding to less than 0.1% Sb is obtained, which could have no possible effect on bulk phase stability. LEED done at the end of this step showed that the 1×1 structure had been preserved during the growth. Figure 1 shows a cross section of this sample and electron diffraction and LEED patterns corresponding to the different layers. It is clear from this picture that the top layer, grown on the 1×1 surface, does not show any ordering, while the bottom layer shows the "usual" order.

The fact that simply changing the surface reconstruction from a 2×1 to a 1×1, on the same sample, changes the resulting alloy phase clearly demonstrates that the ordering is entirely due to surface factors. While this rules out previous explanations of the ordering, we propose a mechanism which can account for virtually all of the experimental findings to date. In this picture, the ordering is associated with local segregation induced by stresses at the surface.

Subsurface strains in the Si(001) dimer-reconstructed surface were first studied in a Keating model by Appelbaum and Hamann.[10] In order to form a dimer, two atoms initially separated by 3.84 Å, move together to form a bond with a 2.3–2.4 Å bond length. In the process the backbonds of these two surface atoms are strongly bent. Large strains (and associated stresses) were found down to the fifth layer of the sample.

A cross section of the dimer structure is shown in Fig.

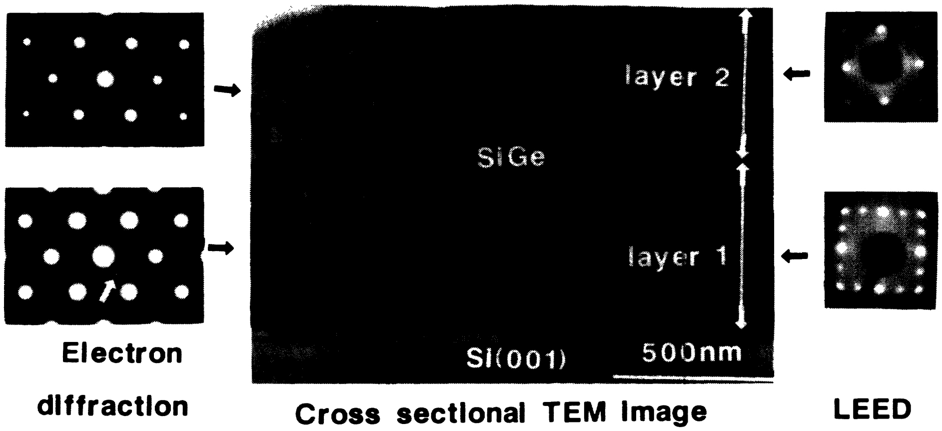

FIG. 1. Cross-sectional view, and corresponding electron diffraction and LEED patterns, for the sample used to determine the importance of the specific reconstruction. Both layers are $Si_{0.5}Ge_{0.5}$, but layer 1 was grown on bare Si, while layer 2 was grown on Si saturated with Sb. The LEED patterns show the change from a 2×1 reconstruction to a 1×1 structure. The LEED patterns were taken before and after growth of each layer. On the diffraction pattern, the arrow indicates one of the extra spots due to ordering present in the bottom layer only.

2(a). It was recently pointed out by Kelires and Tersoff[11] that, as illustrated in Fig. 2(a), alternating atoms in both the third and fourth layers of the sample are under compressive or tensile stress. These atomic-scale stresses can give rise to site-specific segregation in the alloy. Atomic sites under compressive stress would rather be occupied by Si (which has a smaller atomic radius), while sites under tensile stress prefer Ge (which has the larger radius).

In Fig. 2(b) we show a situation in which a double layer has grown on top of the initial surface. Again, there is an alternation of Si-rich and Ge-rich pairs in the third and fourth layers of the crystal. Assuming that the elemental distributions in the subsurface layers are fixed when a new double layer is formed (based on the very low bulk diffusion coefficients at the growth temperature), one can easily see how alternating double layers are Si and Ge rich, respectively, giving rise to long-range ordering of the bulk film after prolonged growth. The order is of the SiSi-GeGe type observed experimentally, rather than the SiGe-GeSi type predicted at low temperature by theory.

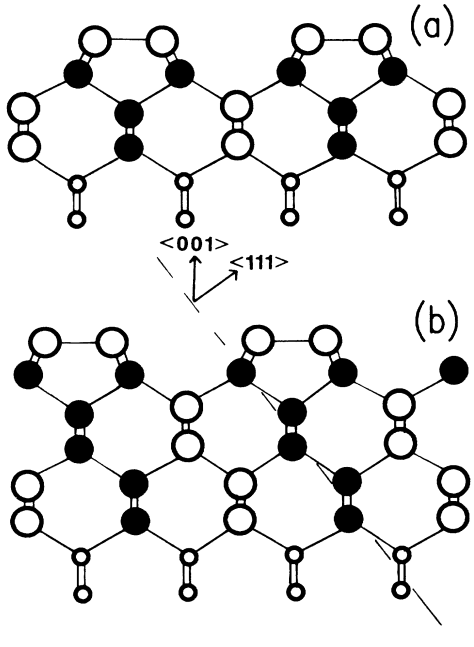

FIG. 2. (a) Cross section of the (001) 2×1 surface, projected onto a (110) plane. Surface dimers are at the top. Large solid circles correspond to sites under compressive stress, favoring Si occupancy. Large open circles denote sites under tensile stress, favoring Ge. (Dimer sites are also shown as large open circles, despite their small stress, because the surface energy favors Ge occupancy for those sites.) Small circles denote sites with little preference for Si or Ge. (b) Proposed growth process: The third and deeper layers in (a) are assumed immobile, while two more layers are added. Thus the circles in the fifth and sixth layers denote Si or Ge occupancy due only to kinetics (past history), rather than to actual stress or any equilibrium preference.

Based on the above scheme, one would expect to find four domains: Two domains are due to the fact that the 2×1 surface has a two-domain surface reconstruction. In addition, for each 2×1 domain there are two equivalent ⟨111⟩ planes that intersect the surface. This has been shown to be true experimentally by LeGoues, Kesan, and Iyer.[1]

One may ask why the ordering should persist along a specific set of ⟨111⟩ planes, instead of zigzagging back and forth, which would result in arbitrarily small domains, unlike the large micron-size domains observed.[1] Using the method described in Ref. 12, we have calculated the energy difference between continuing the ⟨111⟩ ordering and reversing the registry. The calculated energy difference is about 80 meV per dimer. This is a very large difference, since the 2×1 reconstruction requires switching an entire surface domain and not just a single dimer. Thus zigzagging is energetically quite unfavorable.

The ordering mechanism described above immediately accounts for the fact that the ordering disappears for different growth orientations, or even for a different surface reconstruction induced by an adsorbate. It also explains why, once destroyed by annealing, the order cannot be recovered. This disappearance of ordering as the growth temperature increases can also be explained since, as shown by Kelires and Tersoff,[11] the equilibrium segregation decreases significantly as the temperature increases.

The range of temperature for which order strong enough to be detected is observed here is significantly higher than was predicted by Kelires and Tersoff. Since it is difficult to gauge quantitatively how accurately the stress is described by the empirical classical potential they used, and since their calculation referred only to thermodynamic equilibrium, this discrepancy is not surprising.

It is worth noting that only two assumptions were necessary to establish our model. First, it is important that the growth occur by the motion of double steps, to permit large domains of a single ⟨111⟩ ordering direction. Although this has not been experimentally verified for this system, it has been shown to be the case for Si grown on Si(001) in the same range of temperature.[13] The second assumption concerns the fact that there is enough diffusion at the third and fourth layers to establish a near equilibrium segregation, but that diffusion below the fourth layer is negligible so that, once established, the segregation is "frozen." Again, this assumption can be addressed at least qualitatively: Bulk diffusion is negligible at the growth temperature. On the other hand, the surface layers are under considerable stresses, and it is known that diffusion can be enhanced by several orders of magnitude by stress.[14] Furthermore, since the growth occurs by the motion of double steps across the surface, most of the diffusion necessary to obtain the observed order would have to occur at these steps where surface, rather than bulk, diffusion operates.

In conclusion, we have shown that ordering in SiGe is determined strictly by the surface growth, and not by bulk equilibrium as was believed. We attribute the ordering to microscopic stresses associated with the 2×1 reconstruction of the growth surface. All previous experimental results[1-4] can be explained this way (except for the reversibility of the order-disorder transition claimed by Ourmazd and Bean).

This model also explains some of the more nagging discrepancies between experiment and theories that claimed that bulk stresses could account for the ordering: Lockwood *et al.*[4] mentioned that, in at least one sample, ordering was observed for thick films, where no strain was expected, and Müller *et al.*[3] did note that "ordering occurs independently of the strain distribution in the layers." Finally, the model explains why the "wrong" phase is observed, i.e., not the phase with the lowest calculated bulk energy.

We would like to thank R. Griffin and B. Ek for their technical assistance.

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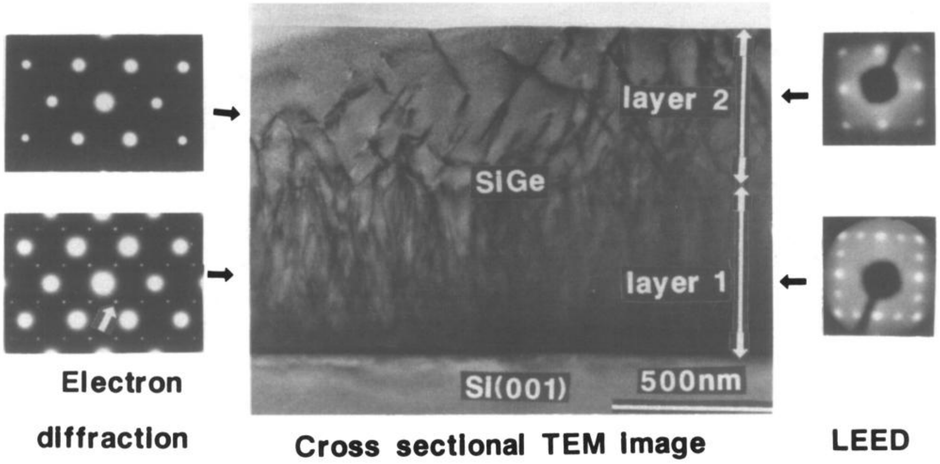

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