7×7 Reconstruction of Ge(111) Surfaces under Compressive Strain

H.-J. Gossmann, J. C. Bean, L. C. Feldman, E. G. McRae, and I. K. Robinson
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 25 March 1985)

We have discovered a correlation between lateral compressive strain in an elemental material and the reconstructed state of its surface. We studied continuous films of pure Ge epitaxially grown on Si(111) substrates. The in-plane lattice parameter varies continuously with film thickness while the surface symmetry changes from $c2\times 8$ to 7×7. The results indicate an important role of lateral compressive stress in the 7×7 reconstruction.

PACS numbers: 68.20.+t, 61.14.Hg, 61.80.Mk, 68.55.+b

From the earliest observation of reconstruction at semiconductor surfaces investigators have speculated on the role of stress in the spontaneous breaking of symmetry at a crystal surface. Recently a number of authors have suggested mechanisms in which stress is a driving force for surface reconstruction[1-3]; the most stable reconstructed state of a surface therefore should be determined by the amount of strain in the crystal. A controlled experiment to demonstrate the direct influence on reconstruction of strain caused by *external* stress is difficult in view of the very large forces required over the cross-sectional area of a massive crystal. Thin semiconductor films, however, have been previously shown to be highly strained when grown eptiaxially on substrates of dissimilar lattice constant[4]; the strain can be controlled by variation of either film composition or thickness. We report on the use of thickness dependence of strain to vary the lateral compression of pure Ge films and the observation of a remarkable transition from the normal $c2\times 8$ structure[5,6] of annealed Ge(111) in less-strained films to the radically different Ge(111)-7×7 structure for more-compressed films.

The growth of epitaxial semiconductor films on a different semiconductor substrate—a heterostructure—is an area of intense current interest. Successful epitaxy has been achieved[7] in systems such as AlGaAs/GaAs where the lattice constants of the film and the substrate differ by less than 0.1%. More recently[4,8] there has been an increasing interest in lattice-mismatched systems, often with the employment of alloys, where the lattice constants of the semiconductor pair can differ by as much as 3%. The growth of these "strained layer" structures follows the general description of the epitaxial growth process first given by van der Merwe and co-workers.[9] In this model thin layers grow pseudomorphically (with the same in-plane lattice constant as the substrate) to a maximum "critical" thickness. In thicker films the strain energy is relieved by misfit dislocations; such films contain some residual strain but less than that associated with the maximum in the pseudomorphic state. As the film thickness increases the average strain decreases and the film lattice constant tends towards that of the overlayer material. Strained films, either pseudomorphic or partly relieved, can display a variety of interesting properties in solid-state science, including novel surface structures, which is the topic of this Letter. Here it is advantageous to choose an elemental rather than alloy or compound system to avoid difficulties of segregation or disproportionation and to allow a straightforward comparison with surfaces of bulk crystals.

The principal finding reported here is that thin films of pure Ge grown by molecular-beam epitaxy (MBE) on Si(111) show an abrupt change in the reconstructed state of their surfaces, as seen in low-energy electron diffraction (LEED) patterns observed *in situ*. The change is from a newly discovered 7×7 state[10] on the thinnest films to the familiar $c2\times 8$ structure known for unstrained annealed Ge(111) surfaces.[5,6] We conclude that it is the lateral stress, evident in the strain of these films, that determines the equilibrium state of their surfaces.

In our experiments Ge films of varying thickness were grown by MBE on Si(111)-7×7 substrates at 3 Å/s and 550 °C.[4] The surface periodicity was monitored at room temperature after each Ge deposition by an *in situ* display LEED apparatus. Measurement of the strain must be carried out in the region adjacent to the surface of the film since misfit dislocations can give rise to a variation of lattice constant through the depth of the film. A technique that combines high absolute accuracy with surface sensitivity is therefore required. We chose glancing-incidence x-ray diffraction[11] as the most suitable technique. Here the sample surface plane is oriented almost parallel to the diffraction plane of a four-circle x-ray diffractometer which causes both incident and diffracted rays to make glancing angles ($< 1°$) with the surface. Refraction of the x rays close to the critical angle (0.2° for Ge) allows in-plane Bragg reflections to be sampled while penetration into the film is limited to ~ 100 Å. The in-plane lattice parameter of the film, a_{film}, is then determined directly from the position of the $[4\bar{4}0]$ Bragg reflection. The compressive strain, ϵ, is calculated as the fractional difference from $a_{\rm bulk}$, the lattice parameter for bulk Ge:

$$\epsilon = (a_{\rm bulk} - a_{\rm film})/a_{\rm bulk}. \quad (1)$$

The measured surface strain, as well as the reconstructed state, are shown as a function of film thickness in Fig. 1. The thinnest (100 Å) films had a strain of $(0.40 \pm 0.05)\%$, which is much less than the 4.01% corresponding to the pseudomorphic growth of Ge on Si. These films must therefore contain a high density of dislocations at the Si/Ge interface. Nevertheless, the quality of the epitaxy was high, with film mosaic spreads always less than 0.5° FWHM. Thicker films were progressively less strained, and had a completely relaxed lattice parameter after 3000 Å. In the series of samples shown in Fig. 1, the reconstruction switches between 1000 and 1500 Å, or between strains of 0.36% and 0.22%, which indicates that there is a critical strain between these limits. Another series, with different growth conditions, showed quantitative differences in the thickness dependence of strain. However, the critical strain associated with the change of LEED pattern, this time in a film 750 Å thick, was found to be the same. Thus we find that surface reconstruction correlates with strain and not with film thickness.

Control experiments to exclude the possibility that the Ge(111)-7×7 structure is induced by mechanisms unrelated to strain were performed before further characterization of the 7×7 reconstruction. These experiments are discussed in the following paragraphs. For this purpose, samples were transferred in air to different experimental stations.

Composition and morphology of the films were analyzed by grazing-exit-angle Rutherford backscattering spectrometry (RBS),[12] secondary-ion mass spectrometry (SIMS), and Auger-electron spectroscopy (AES). No surface preparation was done between growth in the MBE system and analysis. From the RBS measurement, we obtained an upper limit of less than 1 monolayer of Si surface segregation. For the density of Si atoms in the Ge overlayer SIMS gave an upper limit of $\ll 10^{19}$ cm^{-3}. AES indicated only the presence of Ge in the surface, with dilute amounts of O and C, but no Si. After two sputter (4×10^{15} cm^{-2} Ar ions, 1 keV, grazing incidence, room temperature) and anneal (20 min at 670 K and 10 min at 800 K) cycles the sample surface showed no contamination greater than 0.01 monolayer.[13] These results show that Ge was present as a continuous film and that there was neither segregation of Si to the surface nor intermixing. Moreover, the absence of Si signals in our AES measurement specifically indicates that the Ge overlayer does not form "islands," i.e., agglomerates of Ge with exposed patches of Si substrate in between, as can happen under other growth conditions.[14] This eliminates the possibility that the observed 7×7 structure originates from the Si substrate.

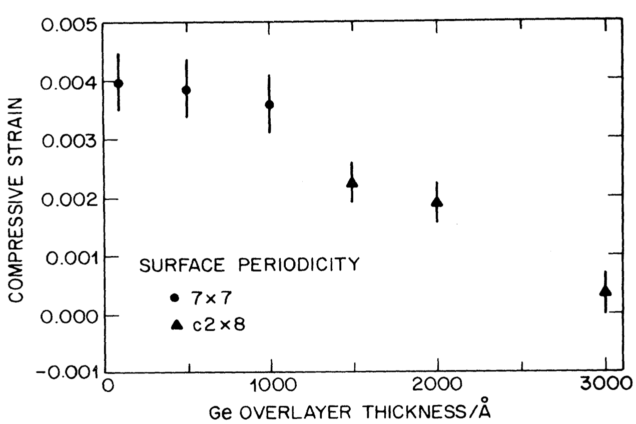
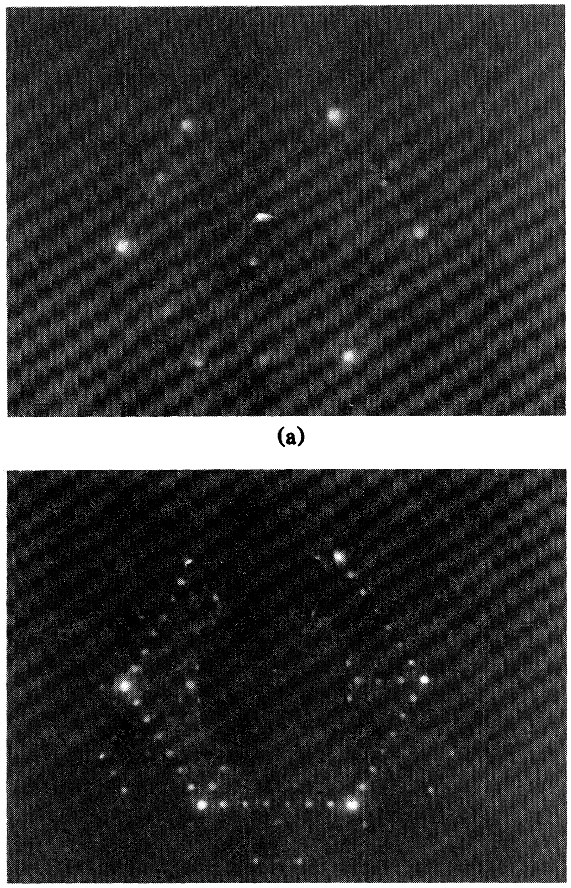


FIG. 1. Lateral compressive strain $\epsilon = (a_{\rm bulk} - a_{\rm film})/a_{\rm bulk}$ ($a_{\rm film}$ denotes the average in-plane lattice constant of a Ge film and $a_{\rm bulk}$ the Ge bulk lattice constant) as a function of Ge overlayer thickness. Different symbols denote the different surface symmetry of the films observed by *in situ* LEED immediately after growth.

We can also exclude the possibility that the observed Ge-7×7 reconstruction is somehow a copy of a 7×7 "template" of the substrate. X-ray diffraction shows that the Ge film does not adopt a new structure upon straining but suffers a simple hexagonal distortion; there is no 7×7 periodicity in the bulk of the film. Furthermore, previous RBS-channeling experiments[15] showed that when more than 3 monolayers of Ge are grown on Si(111) above room temperature the underlying Si substrate reorders to a bulklike structure that does not contain the displaced monolayers characteristic of the 7×7 reconstruction. When Ge-7×7 films are sputtered, the reconstructed LEED pattern disappears. Subsequent annealing, however, restores the 7×7 pattern spontaneously, which shows that it is the equilibrium state of the strained film, and not a metastable copy of a template.

For more extensive characterization of the Ge(111)-7×7 structure, LEED patterns were obtained after the sputtering and annealing of 500-Å films following transfer in air. In some cases superposed 7×7 and $c2\times8$ patterns were observed. Prolonged sputtering was found to weaken the 7×7 in favor of the $c2\times8$ component. Figure 2 shows 7×7 patterns from our Ge films and also a Si substrate. The distribution of intensity among the $\frac{1}{7}$-order spots is practically identical, which indicates that Ge-7×7 and Si-7×7 structures are very similar. Ion-beam crystallography[16] was performed on a 500-Å film prepared as above: Ge surface peak measurements were carried out with 1.0-MeV He$^+$ ions and resulted in 3.13 ±0.17 atoms/row in normal ⟨111⟩ incidence and 4.61 ±0.20 atoms/row in off-normal ⟨11$\bar{1}$⟩ incidence.[17] The number of



(a)

(b)

FIG. 2. LEED patterns in normal incidence. (a) Ge(111)-7×7 of a strained 500-Å film, electron energy 33 eV; (b) Si(111)-7×7, 35 eV.

monolayers displaced because of the Ge-7×7 reconstruction is thus larger in off-normal $\langle 11\bar{1}\rangle$ incidence than in normal incidence. This same result is found for the Si(111)-7×7 surface,[18] and is further evidence of structural similarity between Ge-7×7 and Si-7×7 surfaces.

All of these experimental results confirm that we have created a strained Ge film which is uniform and pure and which displays a surface with the same atomic periodicity and a structure similar to that of the Si(111)-7×7 surface. This observation unifies our picture of elemental semiconductor surface structures. It is known that the (100) surfaces of both Ge and Si display $c4\times2$ periodicity.[19,20] Similarly the cleaved (111) surfaces of Si and Ge both show 2×1 periodicity.[5] It is an interesting enigma that the annealed (111) surfaces show *different* surface periodicities,[5,6,19,21] although other aspects of the surfaces are similar. The results presented here indicate that surface periodicity is a subtle function of strain; we can regard strain, like temperature,[22] as an experimental variable that determines reconstruction.

Our observation of a clean Ge(111)-7×7 surface may be related to the 7×7 state seen first by Ichikawa and Ino[23] after the annealing of 0.3–0.5 monolayer of Sn on Ge(111)-$c2\times8$. It is not clear at present whether Sn is substituted for Ge in this system,[24] but if it were, the Sn-Ge covalent bonds would be under compressive strain relative to those of a clean Ge(111) surface.[3] The diffraction patterns of Ge(111)-7×7/Sn (Ref. 23) and of the compressed Ge(111)-7×7 surface are both identical to those of Si(111)-7×7, which implies that the three structures are homologous. Thus we can regard the Ge(111)/Sn surface as an analog of compressed Ge(111) and its formation of a 7×7 state as strain mediated.[3]

An important role for lateral compressive forces has already been proposed in the context of a particular model of the Si(111)-7×7 reconstruction.[2,25] In this "triangle-dimer stacking-fault" model, stress is relieved by surface dislocations forming a 7×7 network.[26] The observation of a Ge(111)-7×7 reconstruction fits into this picture if it is assumed that the extra compressive stress supplied by the Si(111) substrate, which results in straining of the films, is necessary and sufficient to generate the surface dislocation network.

In conclusion, we have discovered that the 7×7 surface reconstruction of Ge films grown on Si(111) correlates with film strain and that this can be varied by control of the overlayer thickness. LEED and high-energy ion scattering indicate a close structural similarity between the Ge and Si 7×7 surfaces. These results demonstrate for the first time the correlation between strain and mode of reconstruction. In particular, the dependence of the surface symmetry on the lateral contraction in pure Ge supports the hypothesis that the 7×7 reconstruction is promoted over the $c2\times8$ by lateral compressive forces.

We acknowledge the technical assistance of R. A. Malic, R. T. Lynch, and W. K. Waskiewicz. The SIMS analysis was provided by L. C. Hopkins.

[1]J. C. Phillips, Phys. Rev. Lett. **45**, 905 (1980).

[2]E. G. McRae, Phys. Rev. B **28**, 2305 (1983).

[3]T. Ichikawa and S. Ino, Surf. Sci. **136**, 267 (1984).

[4]J. C. Bean, L. C. Feldman, A. T. Fiory, S. Nakahara, and I. K. Robinson, J. Vac. Sci.Technol. A **2**, 436 (1984).

[5]J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. **34**, 2298 (1963).

[6]P. W. Palmberg and W. T. Peria, Surf. Sci. **6**, 57 (1967); D. J. Chadi and C. Chiang, Phys. Rev. B **23**, 1843 (1981).

[7]A. C. Gossard, in *Treatise on Materials Science and Technology,* edited by K. N. Tu and R. Rosenberg (Academic, New York, 1982), Vol. 24.

[8]G. C. Osbourn, J. Appl. Phys. **53**, 1586 (1982), and Phys. Rev. B **27**, 5126 (1983).

[9]F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. London, Ser. A **198**, 216 (1949); J. H. van der Merwe, J. Appl. Phys. **34**, 123 (1963).

[10]H.-J. Gossmann, J. C. Bean, L. C. Feldman, E. G. McRae, and I. K. Robinson, J. Vac Sci. Technol. A (to be published).

[11]W. C. Marra, P. Eisenberger, and A. Y. Cho, J. Appl. Phys. **50**, 6927 (1979); I. K. Robinson, Phys. Rev. Lett. **50**, 1145 (1983).

[12]W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).

[13]While this treatment produced a pure Ge surface, annealing at higher temperatures (10 min at 950 K) did lead to segregation of Si to the surface.

[14]A. G. Cullis and G. R. Booker, J. Cryst. Growth **9**, 132 (1972); E. Kasper, H. J. Herzog, and H. Kibbel, Appl. Phys. **8**, 199 (1975).

[15]H.-J. Gossmann, L. C. Feldman, and W. M. Gibson, Surf. Sci. (to be published).

[16]L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).

[17]The expected value for a bulklike terminated surface would be 2.52 atoms/row, based on a one-dimensional root mean square vibrational amplitude of 0.087 Å, no surface enhancement of vibrations, and correlation coefficients of 0.0 for long and 0.475 for short distances along a $\langle 111 \rangle$ string (O. H. Nielsen, unpublished).

[18]R. J. Culbertson, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **45**, 2043 (1980).

[19]J. J. Lander and J. Morrison, J. Chem. Phys. **37**, 729 (1962), and J. Appl. Phys. **34**, 1403 (1963).

[20]M. J. Cardillo and G. E. Becker, Phys. Rev. Lett. **40**, 1148 (1978); T. D. Poppendieck, T. C. Ngoc, and M. B. Webb, Surf. Sci. **75**, 287 (1978); M. Aono, Y. Hou, C. Oshima, and Y. Ishizawa, Phys. Rev. Lett. **49**, 567 (1982).

[21]R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959).

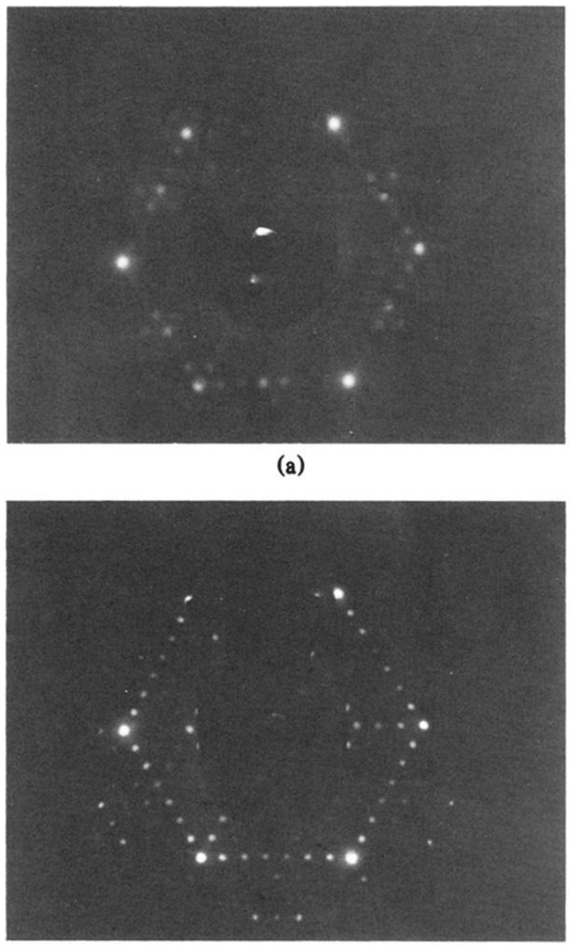
[22]P. A. Bennett and M. B. Webb, Surf. Sci. **104**, 74 (1981); R. J. Phaneuf and M. B. Webb, Surf. Sci. (to be published).

[23]T. Ichikawa and S. Ino, Solid State Commun. **27**, 483 (1978), and Surf. Sci. **105**, 395 (1981).

[24]S. B. Dicenzo, P. A. Bennett, D. Tribula, P. Thiry, G. K. Wertheim, and J. E. Rowe, Phys. Rev. B **31**, 2330 (1985).

[25]E. G. McRae, Surf. Sci. **147**, 663 (1984).

[26]It was suggested (Refs. 2 and 25) that the stress is generated by the backbonding of surface atoms to atoms directly beneath them in a faulted structure. However, recent computer modeling of Si(111) surfaces has indicated very high, lateral compressive stress even in ideal, unfaulted 1×1 structures (E. Pearson, T. Takai, T. Halicioglu, and W. A. Tiller, unpublished).



(a)

(b)

FIG. 2. LEED patterns in normal incidence. (a) Ge(111)-7×7 of a strained 500-Å film, electron energy 33 eV; (b) Si(111)-7×7, 35 eV.