Observation of Order-Disorder Transitions in Strained-Semiconductor Systems

A. Ourmazd
AT&T Bell Laboratories, Holmdel, New Jersey 07733

and

J. C. Bean
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 April 1985)

We report the observation of an order-disorder transition in the semiconductor strained-superlattice system GeSi/Si, which doubles the lattice periodicity in a ⟨111⟩ direction. This phenomenon may be representative of a class of order-disorder transitions in strained-semiconductor systems, even when the lattice mismatch is small.

PACS numbers: 81.30.Hd, 61.14.Fe, 61.50.Ks, 73.40.Lq

Order-disorder transitions are both common and well studied in metallic alloys. Appropriate annealing of these systems at temperatures lower than a critical value T_c induces the different constituent atoms to occupy special sites in the lattice, so as to produce long-range order in the resultant structure. The transition can be isostructural, where the lattice type is not changed, or neostructural, giving rise to a different lattice after the transition. These transitions are generally driven by large differences in electronegativity, valence electron number, or, especially, size between the ordering atoms. In a recent seminal paper,[1] long-range order was also shown to be present in the semiconductor system AlGaAs on a GaAs substrate, particularly in materials with a high Al content grown at 700 °C. This ordering was most suprising, because the sizes and electronegativities of Al and Ga are almost equal and bulk phase diagrams indicate that, at the growth temperatures, AlAs and GaAs are fully miscible.

In bulk form, GeSi is a model random alloy in the sense that extremely prolonged anneals of several months at any temperature in the range 177 to 925 °C cannot induce long-range order[2] and the solidus and liquidus melting-alloy curves are fitted very well by ideal-solution theory.[3] Recent work on GeSi/Si strained superlattices (SSL's) has provided some indications of short-range order.[4,5] In this paper we report the first observation of a neostructural order-disorder transition in the GeSi/Si strained-superlattice system, which produces major changes in the structure of the alloy layers, leading to a high degree of order in the alloy. We have obtained strong evidence that the order-disorder transition is strain driven and stabilized. We briefly point out the possible effects of this structural change on the optical and electronic properties of this system and the implications of strain in inducing long-range order in other semiconducting systems.

We have studied $Ge_xSi_{(1-x)}$ strained superlattices grown by molecular beam epitaxy on [100] Si as described elsewhere.[6,7] At present we restrict the discussion to a twenty-period superlattice grown at 550 °C, each period consisting of 75 Å of $Ge_{0.4}Si_{0.6}$ and 225 Å of Si. The strain in this system is accommodated almost entirely in the alloy layers and produces a tetragonal distortion of the unit cell.[6] We postpone the discussion of other compositions until a more detailed publication. Careful microscopic examination of the GeSi/Si SSL's studied in the present work by us and others[8] has shown them to be entirely devoid of extended defects and to possess commensurate GeSi/Si interfaces. The samples were annealed in an Ar atmosphere in the temperature range 350–550 °C and cooled at various rates, or quenched in diffusion pump oil. [011] and [001] cross-sectional samples were mechanically polished and ion-beam milled, the milling damage being removed by final irradiation with 2-keV Ar ions. This treatment, used routinely in electron microscopy, allows the examination of the bulk of the sample, with minimum interference from the residual surface damage.

Figure 1 is an electron-diffraction pattern at the [011] pole of a sample annealed for 30 min at 450 °C and cooled at a rate of 2 °C/min. In addition to the reflections due to the normal diamond lattice, two features are noteworthy: (i) the presence of substantial streaking through all the spots including the undiffracted beam and (ii) the occurrence of "extra" reflections at $\frac{1}{2}(111)$, $\frac{1}{2}(311)$, $\frac{1}{2}(331)$, etc., positions. Table I summarizes the intensity of these reflections after various annealing treatments. It is clear that the appropriate anneal can cause the presence of these reflections with significant intensity. Indeed, it is difficult to prevent their occurrence, although they can be easily overlooked as a result of their weak intensities. These extra reflections occur most strongly when the sample is annealed at 450 °C and cooled at 2 °C/min. They can be made to disappear by subsequent annealing at 550 °C and quenching. Further annealing at 450 °C and slow cooling causes their reappearance, thus showing their occurrence to be reversible. Significantly, no reflections of the type (100) or (110) were observed, either at the [001] or [011] pole.

The streaking parallel to the [100] growth direction through all the reflections is present in all the samples, including the as-grown ones. Since the length of the streaks does not increase with the diffraction vector and the undiffracted beam also displays streaking, strain can be ruled out as a possible origin. The streaks must therefore be due to sheetlike inhomogeneities in the sample. Although the presence of interfaces in the superlattice may be considered as a possible explanation, streaks are not observed in other superlattice systems, and their origin must be sought elsewhere. Indeed, as the broadening and streaking of reflections often act as the precursors for the appearance of superstructure reflections in ordering metallic systems,[9] it was the presence of these streaks which alerted us to the possible presence of inhomogeneities such as antiphase domain boundaries and, hence, long-range order. The "extra" spots are best observed in regions of crystal between 150 and 600 Å thick. Their presence is masked by diffuse scattering in thicker regions of the foil.

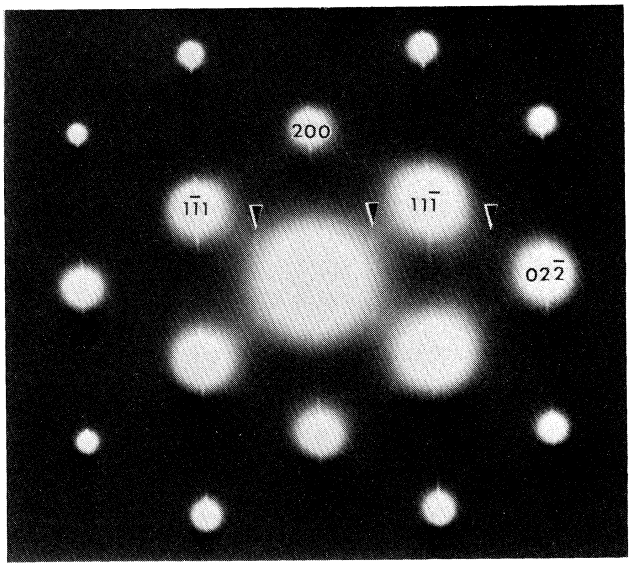

FIG. 1. Electron diffraction pattern of an ordered GeSi/Si superlattice near the [011] pole. Note the superstructure reflections and the streaks through all the spots.

Since no reflections allowed by the diamond or fcc lattices can occur at positions such as $\frac{1}{2}(111)$, etc., their presence and behavior provide a clear indication of a reversible structural change upon annealing. Furthermore, since the intensities of these reflections depend on the annealing procedure and in particular the cooling rate, a mere change in the spacing between alternate {111} planes, for example because of a Jahn-Teller distortion (which is spontaneous), is unable to serve as an explanation. The observed structure deduced from our studies can be described in detail by a superposition of domains with pseudodiamond structure, in each of which the stacking in a single ⟨111⟩ direction consists of (111) planes composed entirely of one atom type in the sequence SiSiGeGeSiSiGeGe. . . (Fig. 2). Although the ordering is expected to produce a slight trigonal distortion of the unit cell, this distortion is not measurable by electron diffraction. In the following, therefore, we treat the ordered structure of each domain as cubic, with a doubled periodicity in a ⟨111⟩ direction. The corresponding primitive unit cell has the axes $(a/2)[1\bar{1}0]$, $(a/2)[0\bar{1}1]$, $a[101]$, and

TABLE I. Summary of the effect of annealing on the superstructure reflection intensity.

Anneal temperature (°C)	Anneal time (hr)	Cooling rate (deg/min)	$\frac{1}{2}(111)$ intensity
As-grown	$\sim\frac{1}{4}$ (growth time)	~ 100	very weak
350	$\frac{1}{2}$	quenched	very weak
400	$\frac{1}{2}$	quenched	very weak
450	$\frac{1}{2}$	quenched	weak
450	$\frac{1}{2}$	~ 100	medium
450	$\frac{1}{2}$	2	strong
450, 430	$\frac{1}{2}$, 16	2	medium
450	$\frac{1}{2}$	0.3	medium
500	$\frac{1}{2}$	quenched	weak-medium
500	$\frac{1}{2}$	2	weak-medium

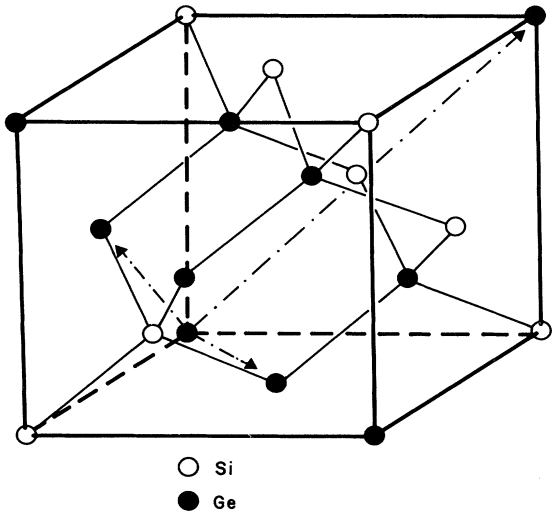

FIG. 2. Structure of the ordered GeSi alloy, where pairs of widely spaced {111} planes are occupied by the same atom types. It is also in principle possible for the closely spaced {111} planes to be so occupied. The arrows represent the primitive unit cell axes.

contains two Si and two Ge atoms. The structure factor is (with the usual symbols)

$$S = 2\cos\{2\pi\mathbf{g}\cdot(a/8)[111]\} \times\{f_{\mathrm{Si}}+f_{\mathrm{Ge}}\exp 2i\pi\mathbf{g}\cdot(a/2)[101]\}.$$

S is zero for all reflections (hkl) with $h+k+l=4n+2$ and is proportional to $f_{\mathrm{Si}}-f_{\mathrm{Ge}}$ for "superstructure" reflections such as $\frac{1}{2}(111)$. The observed diffraction pattern is a superposition of the contributions from the four possible domain orientations (as well as the Si layers). The only superstructure reflections to be observed from the above structure are of the type $\frac{1}{2}(111)$, $\frac{1}{2}(311)$, and $\frac{1}{2}(331)$, etc. In particular, reflections of the type (100) and (110) remain forbidden in the ordered structure. These features are in exact agreement with our observations. With the assumption of an order parameter of one (i.e., complete and perfect ordering of the GeSi layers) the maximum theoretical intensity of a $\frac{1}{2}(111)$ reflection is $\frac{1}{600}$ of a (111) reflection. This is calculated as follows. (i) The GeSi layers are $\frac{1}{3}$ as thick as the Si layers. (ii) The ordered GeSi has four possible domain orientations, so that only $\frac{1}{4}$ of the GeSi contributes to each $\frac{1}{2}(111)$ reflection, while the entire volume of the strained superlattice contributes to the (111) reflections. (iii) Given the composition of the layers, the ratio of the structure factors $\frac{1}{2}(111)/(111)=\frac{1}{7}$, the intensity ratio being proportional to the square of the structure factor. The product of these factors, namely $\frac{1}{3}\times\frac{1}{4}\times\frac{1}{7}^2$, yields the estimate that the $\frac{1}{2}(111)$ superstructure reflection has a maximum theoretical intensity $\frac{1}{600}$ of the (111) reflection under our observation conditions. By photodensitometry of plates of different exposure, we find that the experimentally observed $\frac{1}{2}(111)$ intensity approaches this value for the sample of Fig. 1. This indicates that a substantial degree of long-range order can be achieved by annealing at 450 °C and slow cooling.

It is clear from Table I that even quenching from 500 °C is unable to produce a totally disordered system. Thus the as-grown samples (which are not quenched after growth) must also be to a small degree ordered. This has been interpreted by previous workers as short-ranged order,[4,5] but in reality represents the initial stages of the establishment of long-range order. As in the case of ordering metallic systems,[9] we believe that the streaks are indicative of the onset of order in the GeSi alloy layers, although the associated superstructure reflections can be too weak to be clearly observable.

The structure described above is most unusual and can be related only to the ordered form of CuPt, which has a fcc lattice.[10] The GeSi alloy orders similarly, in the sense that each fcc sublattice of the diamond lattice resembles the ordered CuPt structure. Although it is difficult to obtain dark-field images of the ordered GeSi system by use of the weak superstructure reflections, we can draw crystallographic analogies between the GeSi and CuPt systems to infer the microstructure of the ordered GeSi system. CuPt orders into laminar twinned regions.[11] The observation of the streaks parallel to the [100] direction thus indicates the presence of laminar ordered domains in the GeSi system. Since the domains must grow upon annealing, but the length of the streaks does not diminish with annealing, the streaks are probably due to the boundaries between the ordered laminar domains, rather than the shape of the domains themselves.

It is noteworthy that the order decreases after prolonged annealing and is not observed in the thinnest regions of electron transparent foils. Prolonged annealing reduces the stress due to Ge out diffusion from the alloy layers. The stress is also able to relax in thin foils[12] and the ordered thinned layer is superheated during the thinning process, becoming disordered by the energy input from the incident ion beam. In either case the relaxation of the stress reduces, or totally destroys, the long-range order. This lends strong support to the notion that the ordering transition is strain driven and stabilized. We believe that this mechanism may be operative in other semiconductor alloy systems. In particular, it may be the cause of the ordered state in the AlGaAs/GaAs system, where maximum order was observed, not at the stoichiometric composition of $Al_{0.5}Ga_{0.5}As$, but in $Al_{0.75}Ga_{0.25}As$, which, of the samples studied, provided the largest lattice mismatch with the GaAs substrate.[1] Although it may be argued that the mismatch in the AlGaAs/GaAs sys-

tem is small, it must be borne in mind that, as a result of the large thickness of the ternary layers studied, substantial strain energy had been present.

On a microscopic scale we note that (111) double-layer ordering provides the possibility for each Si atom to have three Ge and one Si nearest neighbors (and vice versa), as shown in Fig. 2. The Si layers are then unstrained relative to the substrate, while the Ge layers are uniaxially strained. The transverse acoustic modes of Ge at the $\langle 111 \rangle$ zone boundary are softer (normalized to the optic mode frequency) than the corresponding Si modes.[13] The difference is small, as is the lattice mismatch between AlAs and GaAs. The ordering energy may arise from the strain being preferentially accommodated by the Ge atoms; a possibility which exists for the observed ordered structure, but not for a disordered distribution of atomic species.[14]

In conclusion, we have observed a novel ordering transition in GeSi alloy layers in a strained superlattice. This ordering has not been observed in bulk GeSi, probably because of the zero or low value of the transition temperature T_c, which would make the transition impossible, or too slow to observe on laboratory time scales. We have presented persuasive evidence that the substrate stress drives the observed transition and probably increases T_c. Since it is possible that this phenomenon may occur in other strained-semiconductor systems, strain may provide the possibility of tailoring the optical and electronic properties of semiconductors by inducing and controlling the appropriate transformation. In particular, the doubling of the periodicity and the noncentrosymmetry of the ordered unit cell may lead to interesting modifications of the band structure and optical properties of GeSi upon ordering. Discussion of these modifications will be presented elsewhere.

It is a pleasure to acknowledge valuable discussions with A. Bourret, J. M. Gibson, R. Hull, H. Leamy, and particularly P. B. Littlewood, and J. C. Phillips. We are indebted to J. A. Rentschler and R. T. Lynch for expert technical assistance.

[1]T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[2]M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), 2nd ed., p. 774.

[3]C. D. Thurmound, J. Phys. Chem. **57**, 827 (1953).

[4]R. Hull, J. M. Gibson, K. J. Marcantonio, J. C. Bean, and R. People, Bull. Am. Phys. Soc. **30**, 265 (1985).

[5]R. Hull, J. C. Bean, F. Cerdeira, A. Pinczuk, J. M. Gibson, and N. E. Hartsough, to be published.

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

[7]J. C. Bean, in Proceedings of the Fall Meeting of the Materials Research Society Symposium on Layered Structures, Epitaxy, and Interfaces, Boston, 1984, edited by J. M. Gibson (to be published).

[8]R. Hull, J. M. Gibson, and J. C. Bean, Appl. Phys. Lett. **46**, 179 (1985).

[9]R. S. Irani, Contemp. Phys. **13**, 559 (1972).

[10]J. O. Linde, Ann. Phys. (Leipzig) **30**, 151 (1937).

[11]R. S. Irani and R. W. Cahn, J. Mater. Sci. **8**, 1453 (1973).

[12]J. M. Gibson and M. M. J. Treacy, Ultramicroscopy **14**, 345 (1984).

[13]J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 94.

[14]P. B. Littlewood, private communication.

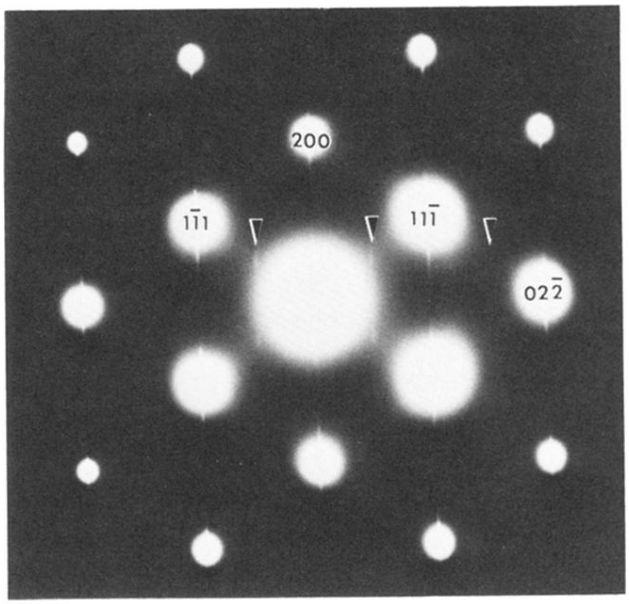

FIG. 1. Electron diffraction pattern of an ordered GeSi/Si superlattice near the [011] pole. Note the superstructure reflections and the streaks through all the spots.