COMPOSITIONAL ORDERING IN SEMICONDUCTOR ALLOYS

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ABSTRACT

Compositional ordering has been observed in a wide variety of III/V semiconductor alloys as well as in SiGe alloys. The thermodynamic driving force is now understood in terms of minimization of the microscopic strain energy of the bonds in the solid. However, the mechanism leading to the specific ordered structures formed is only now beginning to be understood. It appears to be intimately related to the physical processes occurring on the surface during epitaxial growth, specifically surface reconstruction and the attachment of atoms at steps and kinks. Thus, an improved understanding the ordering process may lead to a better understanding of the surface processes occurring during epitaxial growth from the vapor.

This paper will review the current understanding of the ordering process, including discussions of the arrangement of atoms on the surface and the nature of surface steps. The emphasis will be on the use of patterned surfaces to investigate and control the ordered structures formed during organometallic vapor phase epitaxial growth of GaInP. Using photolithography and chemical etching, [110]-oriented steps are formed on the (001) GaAs substrate. The direction of motion of these steps determines the specific variant of the Cu-Pt ordered structure (with ordering on (111) planes) formed. The step density at the edge of the groove apparently determines the degree of order. Highly stepped surfaces suppress ordering or lead to small domains of a single variant. When the steps are very shallow, the large domain of the predominant variant is filled with "inclusions" of the second variant. Step edges that are oriented at nearly 16° from (001) form a \{511\} variant during growth. This facet is observed to grow at the expense of adjacent (001) surfaces and to produce material that is completely disordered.

Growing on intentionally misoriented substrates leads to interesting structures consisting of both large, highly-ordered domains and disordered material. This allows, using cathodoluminescence (CL) imaging, a direct determination of the effect of ordering on the energy band gap. In the GaInP samples studied, the CL images show that the disordered material has a distinct emission pattern consisting of a single, sharp peak at an energy more than 100 meV higher than that observed in the adjacent ordered region.
INTRODUCTION

Atomic-scale ordering is a naturally occurring phenomenon widely observed in III/V alloys as well as for SiGe alloys. This phenomenon, first observed in metallic alloys, involves the formation of monolayer superlattice structures along a particular crystallographic direction in the lattice. In III/V alloys of the type $A_0.5B_0.5C$ or $AB_0.5C_0.5$ three different ordered structures are well documented: Cu-Au ($L1_0$) with ordering on (100) planes, chalcopyrite ($EI_I$) with ordering on (210) planes, and Cu-Pt ($L1_1$) with ordering on (111) planes. The last is by far the most widely observed.

Ordering occurs mainly due to the attempt of the lattice to minimize the microscopic strain energy, produced by short-range statistical compositional fluctuations, inherent in any alloy consisting of atoms with different radii. In the bulk alloy, the lowest energy structure has ordering on (210) planes, followed, in order of increasing energy, by structures with ordering on (100) and, finally, (111) planes. The latter is the highest energy ordered structure, but still has an energy less than that of the disordered material.

Ordering is important for practical reasons. The energy band gap of ordered material with the Cu-Pt structure is predicted to be significantly lower than of disordered alloys. The effect is less pronounced for other ordered structures. The reduction in bandgap was first supported by indirect evidence for GaInP alloys, and recently by more direct evidence provided by cathodoluminescence (CL) spectra measurements of adjacent ordered and disordered regions separated by no more than a few microns. Thus, ordering is to be avoided in short-wavelength lasers and light emitting diodes. On the other hand, a reduction of band gap may be beneficial for InAsSb alloys for infrared detectors operating in the 8-12 μm wavelength regime. It is also expected that by reducing the compositional (and associated band gap) fluctuations in a disordered alloy, ordering may lead to increased free carrier mobilities.

Since many aspects of ordering appear to be kinetically controlled, an examination of the phenomenon may lead to important insights into the surface processes occurring during vapor phase epitaxial growth. The focus of this paper will be an attempt to infer details of these surface processes, such as the surface structure and step motion, from observations of the ordering phenomenon. Since we understand so little about these processes, the conclusions often take the form of questions posed to stimulate and direct the interests of the theoreticians, surface scientists, and epitaxial growth researchers whose expertise will be required to understand these phenomena.

SUMMARY OF SALIENT FEATURES OF EARLIER WORK

1. Ordering is observed in virtually every III/V alloy studied to date as well as in SiGe alloys, as mentioned above.
2. Ordering appears to be confined nearly exclusively to materials grown from the vapor. The strongest ordering appears to occur in materials grown by
organometallic vapor phase epitaxy (OMVPE). It is also observed in materials grown by conventional vapor phase epitaxy (VPE) and molecular beam epitaxy (MBE); however, the degree of order appears to be lower in materials grown by these techniques. A caveat is that this may be partially due to the dissimilar conditions used for the various growth techniques. Ordering is virtually never observed in materials grown by liquid phase epitaxy (LPE) [13].

3. The degree of order and the ordered structure depend markedly on the substrate orientation. With few exceptions, growth on (001)-oriented substrates produces the Cu-Pt structure. Growth on (110) substrates produces material with the Cu-Au structure [14, 15]. Little, if any, ordering is observed for growth on (111) [10, 16], (221), (311) [17], and (511) [18] substrates.

4. Only two variants of the Cu-Pt structure are produced during growth on (001)-oriented substrates, i.e., of the 4 equivalent {111} planes, ordering occurs on only two, (111) and (111). These planes intersect the (001) growth plane along the [110] direction.

5. The presence of [110]-oriented steps on the (001) surface is found to strongly influence ordering. These steps produce only a single variant of the Cu-Pt structure, with steps moving in opposite directions responsible for formation of the two variants observed [1, 9]. This led to the development of a kinetic model that explains the ordering phenomena observed. It is based on the interaction of adatoms with [110] steps on an (001) surface reconstructed to give [110] group V dimer rows.

6. The atomic arrangement on the (001) GaAs surface is well-known from reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) measurements for static GaAs surfaces and also for the surface during MBE growth. For As-rich (001) GaAs surfaces, the results of RHEED [19] and STM [20, 21] measurements agree with theoretical calculations [22] that the surface consists of As dimers running in the [110] direction with every 4th dimer missing, yielding the commonly observed (2x4) structure in the RHEED pattern. The {110} steps are two monolayers high, since the steps separate two flat regions both terminated by [110]-oriented As dimer rows. Static RHEED measurements at higher As pressures yield the c(4x4) structure, where the surface is believed to be terminated by a double layer of As atoms.

Unfortunately, OMVPE does not lend itself to in-situ RHEED analysis since the atmosphere attenuates the electron beam. Thus, until recently, even the most elementary understanding of the III/V surface during OMVPE was missing. It has been postulated that the surface is terminated by H atoms, and hence not reconstructed [23, 24]. This seems extremely unlikely from an epitaxial growth point of view. More direct information has recently become available which also casts doubt on this hypothesis, as discussed below.

Lamelas et al. [25] directly studied (001) GaAs surfaces during OMVPE growth using in-situ surface x-ray scattering from a synchrotron source. The static surfaces heated in the presence of Ga or As reconstruct to form virtually the same structures described above for a UHV environment, i.e., they are not H terminated. However, during OMVPE growth at 575°C, using TMGa and
TBAs, they see no evidence for long range order, i.e., no surface reconstruction. This suggests that the surface during OMVPE is much different than during MBE, where reconstruction persists during growth for most conditions. Naturally, these early results do not rule out reconstruction for other growth conditions.

An optical technique, reflection-difference spectroscopy (RDS)[26], has recently been developed for in-situ characterization of the semiconductor surface. Distinct reflectance difference spectra are observed for each of the reconstructed (001) GaAs surfaces described above. Fortunately, RDS can be used to determine the surface electronic structure even in a non-UHV environment. RDS measurements indicate that the static surface structures at atmospheric pressure under As- and Ga-rich conditions are essentially the same as those seen in the UHV MBE chamber [27]. This suggests that similar reconstructions form during growth of layers by OMVPE and MBE. These measurements indicate that for As-rich conditions the surface is reconstructed to form either the (2x4) or (c4x4) structures with As dimers.

7. Ordering appears to be related to reconstruction of the growing surface. This may be inferred from: i) the crystallographic observations of items 4 and 5, above, combined with the [110] orientation of the dimer rows formed, under certain conditions, on the group V terminated surface of a II/V semiconductor; ii) the absence of ordering in LPE growth where a liquid termination of the surface probably lowers the surface energy, thus eliminating reconstruction; and iii) the formation of the least stable ordered structure during epitaxial growth on (001)-oriented substrates. The absence of order observed for (111)-oriented surfaces would be due to the absence of dimer rows and the absence of order on (311) and (511) surfaces would also be due to the absence of dimers on these highly stepped surfaces consisting of (001) terraces separated by steps. Tsuda and Mizutani [28] report that the 1/2 order streaks due to As-dimer rows observed in RHEED diffraction patterns during MBE growth of GaAs on (001) substrates becomes weaker as the substrate is misoriented from (001) to form (119) and (117) surfaces. The reconstruction would presumably disappear for (115) and (113) orientations, although data are not available.

The conclusion that surface reconstruction plays a key role in the ordering process is supported by recent calculations [29] that show that the presence of both [110] steps and [110] group-V dimer rows on the reconstructed surface favors the formation of the (111) and (111) variants of the Cu-Pt structure. LeGoues et al[2] assert that for the growth of SiGe alloys, ordering only occurs when the surface is reconstructed to form surface dimers. Both the surface reconstruction and ordering are eliminated by heavy Sb doping. However, this conclusion may be doubtful since heavy doping, itself, may be responsible for the lack of order in the resulting layers [30].

Changes in the atomic configuration at [110] steps due to changes in growth conditions, particularly the V/III ratio, may determine the degree of order in the resulting epitaxial layer. Several observations of straight [110] steps for OMVPE growth of GaAs, especially at high As/Ga ratios, have been
reported[31]. For OMVPE growth at low V/III ratios and for MBE growth, in general, the [110] steps are observed to be highly kinked[32].

EXPERIMENTAL RESULTS

Epitaxial layers of GaInP and GaAsP were grown in an effort to better understand the processes occurring on the surface during growth that lead to ordering in the resultant layers. All of the growth studies described were performed in horizontal OMVPE reactors using the group III alkyls trimethylgallium (TMGa) and trimethylindium (TMIn) combined with arsine and phosphine. Ga0.5In0.5P layers are nearly lattice-matched to the GaAs substrates. The GaAs0.5P0.5 layers were grown on thick, VPE-grown GaAs0.6P0.4 “substrates”, since this material is not lattice matched to GaAs.

One approach to studying the effects of step motion on ordering was to produce, photolithographically, in the substrate surface a series of parallel grooves. The purpose of the grooves is to produce surface steps moving in opposite directions on the two sides of the groove. When the grooves are oriented in the [110] direction, the remarkable result is a high degree of order with a single, large domain formed on each side of the groove, as seen in the transmission electron micrographs in Fig. 1. The images were produced using only superspots; thus, the bright regions in each image show the areas with the particular ordered structure indicated. Transmission electron diffraction (TED) patterns show clearly that only the (111) variant is formed on the right-hand side of the groove and that only the (11̅1) variant is formed on the left-hand side. These are the largest domains of ordered material produced to date. The results appear to demonstrate that the [110] step motion has a direct effect on the ordering process. The direction of step motion determines which ordered structure is formed. An alternate interpretation of the data would be that the energies of the two variants of the Cu-Pt structure are dependent on the surface steps. The two interpretations cannot be unambiguously distinguished based on the experimental results. However, the difference is profound. The first is a kinetic interpretation while the second is basically thermodynamic. Certainly, kinetic effects are important. The step propagation velocity partially determines the extent of order produced during growth, since high growth rates produce disordered material[33]. In the remainder of this paper it will be assumed that the direction of step motion is the key factor affecting ordering. However, several phenomena discussed could be interpreted using the thermodynamic approach.

A careful examination of the micrographs in Fig. 1 reveals other interesting features. The triangular region at the bottom of the groove, relatively far from the highly stepped surfaces at the groove edges, contains a mixture of small domains of both variants. This region is seen even more clearly for the GaAsP sample to be discussed below. In this region growth apparently occurs by 2 dimensional nucleation and growth. For any particular island, steps will be moving in both directions; thus, both variants are formed. The lateral extent of
the islands may reflect the density of 2 dimensional nuclei. In addition, the fact that the layers are not a random mixture of monolayer thick domains of the two variants seems to indicate that the nucleation is not random. The direction of step motion must be the same from layer to layer in an individual domain.

An effort was made to determine the effect of groove shape on the ordering observed[9,34]. Using a particular etching procedure[34], shallow, round-bottomed grooves extending laterally to a width of 10 μm were formed with a depth of ∼0.25 μm. The angle between the top surface and the adjacent groove edge is ∼10°. Each side of the groove was found to be strongly ordered with largely a single variant, but with a small volume fraction of the second variant also present. The demarcation line between the two variants was found to meander back and forth laterally as the layer thickness increased. This is believed to be due to changes in the groove shape during the growth cycle. Since the variant formed is believed to be due to the direction of step motion, the position in the groove bottom having the exact (001) orientation determines the point where the two variants meet. For shallow grooves, a slight change in groove shape will alter the position in the groove where the orientation is exactly (001), resulting in the irregular, meandering line of demarcation between the two variants.

The formation of the second variant in a region nominally misoriented to give a single direction of step motion is similar to the observation of two variants in a substrate misoriented by a small angle in the [110] direction. Again, one variant dominates, but regions of the second variant are also observed[35]. Apparently, the step spacing is large enough to allow 2 dimensional nucleation and growth on some terraces.

Deep grooves, up to 1.5 μm deep and 10 μm wide, can also be produced by using the appropriate etching procedure[34]. These grooves, which have an angle between the top surface and the adjacent groove edge of 35°, produce only a single variant on each side of the groove. However, the domains are small. Apparently an intermediate groove shape, with an angle between 10 and 35°, such as that shown in Fig. 1, is optimum for obtaining a high degree of order and a single, large domain on each side of the groove.

Another factor affecting the ordered structure produced is the formation of facets during growth. This is clearly illustrated using GaAs0.5P0.5 layers grown on GaAsP substrates, as seen in Fig. 2[36]. Before discussing the effect of facet growth, several features of Fig. 2 will be compared with the GaInP results of Fig. 1. The triangular region near the center of the groove is very clearly seen to contain both the (111) and (111) variants of the Cu-Pt structure. It is worth noting that the same variants are formed in GaAsP, an alloy with mixing on the group V sublattice, as for GaInP, where the mixing is on the group III sublattice. Also similar to the GaInP layer, shown in Fig. 1, is the presence of single, large domains filling 1/2 of the groove near the surface.

This sample has a remarkable feature not observed in Fig. 1, namely, the chevron-shaped region in the center of the epitaxial layer where the material is completely disordered: This region is dark in both dark-field images. TED
Figure 1: [110] dark field images of GaInP grown on an exactly (001) oriented GaAs substrate patterned with [110]-oriented grooves: (a) image from the 1/2 (111) superspot, (b) image from the 1/2 (111) superspot, and (c) schematic drawing of domains. Arrow "a" indicates the top surface of the GaInP and arrow "b" indicates the GaInP/GaAs interface.
Figure 2: [110] transmission electron microscope images of GaAs$_{0.5}$P$_{0.5}$ grown on an exactly (001) oriented GaAs$_{0.6}$P$_{0.4}$/GaAs "substrate" patterned with [110]-oriented grooves: (a) dark field image from the 1/2 (111) superspot, (b) dark field image from the 1/2 (111) superspot, and (c) bright image of GaAs$_{0.5}$P$_{0.3}$/GaAs$_{0.5}$P$_{0.5}$ superlattice, showing the {511} facets formed at the edges of the groove.
patterns indicate the total lack of ordering in this region. Growth of a GaAs$_{0.5}$P$_{0.5}$/GaAs$_{0.7}$P$_{0.3}$ superlattice structure to show the shape of the groove at various times during growth[36] reveals that {511} facets are formed on each side of the groove during growth, as seen in Fig. 2c. As mentioned above, growth on {511} surfaces produces disordered material.

Closer observation of the TEM cross sections in Fig. 2 reveals other features that add to our understanding of the growth process. The growth rates of the layers in various parts of the groove are quite different. The {511} planes clearly grow at the expense of the adjacent (001) planes. This must be due to surface diffusion of adatoms from the (001) planes to the {511} planes. This is demonstrated by observing the lower growth rate of the (001) planes adjacent to the {511} planes. This leads to a significantly lower growth rate in the triangular region at the bottom of the groove between the {511} planes and to a sloping profile of the surface at the top of the groove near the {511} planes. Even the nominally flat region at the bottom of the groove is sloped to give a convex shape. This can be seen in Fig. 2c, but is more clearly demonstrated by closely observing the dark field images in Fig. 2a and 2b. It is noticed that the left boundary of the triangular region at the bottom of the groove divides a thin (111) domain (on the left) and a thin (111) domain (on the right). This is due to the surface profile changing from a downward slope on the left to an upward slope on the right of the dividing line. The same phenomenon is observed on the right hand boundary of the triangular region. Although less clear, this can also be observed for the GaInP sample in Fig. 1.

These observations indicate that: 1) the Ga and In adatoms have lower energies on the {511} than the {100} crystal faces and 2) the adatom diffusion lengths are considerably longer than 0.1 μm. The higher probability of adatoms sticking to the {511} surface may be related to two factors. One is the step density. Since the atoms have a much lower energy at step edges, at least for {001} faces, it seems reasonable that a more highly stepped surface would have a higher growth rate because it would trap more of the adatoms diffusing across the surface. In this and other studies of growth on non-planar substrates, no evidence of more rapid growth in regions with higher step densities has been clearly observed. The shapes of our curved surfaces seem to remain nearly constant during growth. The shape would change dramatically if the growth rate were higher for regions with higher step densities.

The second and more likely explanation is that the nature of the atoms on the surface is dramatically different for a {511} surface than for a {100} surface misoriented by a few degrees. This is likely due to the disappearance of the surface reconstruction that makes the {001} surfaces so stable. For MBE growth under As-rich conditions, the surface consists mainly of As-dimer rows, forming the commonly observed (2x4) reconstruction discussed above. For Si, the atomic structure of a {511} surface is postulated to be significantly different than for a {100} terrace[37]. In an effort to understand faceting during crystal growth, Bartolini et al[38] suggested that the most stable, "magic" orientations have terrace widths that can accommodate an integer number of reconstruction cells. For an As-terminated {511}B GaAs surface, consisting of 2.9 Å high
[110] steps separated by 10Å terraces, only 2/3 of the surface As atoms would be able to form dimers if the (2x4) reconstructed surface were formed on each (001) terrace. This suggests that the reconstruction forming [110] As-dimer rows on the terraces may be replaced by a lower energy reconstruction. This agrees qualitatively with the results of a RHEED investigation of highly misoriented (001) GaAs surfaces[20]. As mentioned above, observations at the [110] azimuth show weak half-order streaks for As-rich (119) and (117) surfaces. The intensity decreases markedly as the orientation is tilted away from (001). No data are given for (115), but the disappearance of the As-dimers that cause the half-order streaks would seem consistent with their results.

The long diffusion lengths deduced from the groove shapes in Fig. 2c are consistent with observations of similar growth rate non-uniformities for GaAs layers grown by MBE and MOMBE (metal-organic MBE) on patterned substrates[39,40]. From the growth rate profile of the rapidly growing (001) surfaces adjacent to non-growth (111)A surfaces[40] surface diffusion lengths in the [110] direction of the order of a micron were deduced. Interestingly, the direction of diffusion has a significant effect on the diffusion lengths measured[40,41]. The diffusion lengths in the [110] direction, those relevant to the interpretation of the profiles in Fig. 2c, are nearly an order of magnitude longer than those for the [110] direction.

Taken together, these results indicate the facility with which adatoms diffuse across steps. Clearly, the diffusion lengths are very much greater than the step spacings. The results of Hata et al[41] also indicate that the interactions of adatoms is considerably stronger with [110] steps than with [110] steps during MBE growth of GaAs at 560°C. The postulated absence of As dimer rows on the terraces of an As-rich {511}B GaAs surface may also explain the observed absence of ordering for growth on the {511} facets. The ordering models of Stringfellow and Chen[1] and Ogale and Madhukar[29] require both [110] steps and [110] group V dimer rows for the formation of the two observed variants of the Cu-Pt structure, as discussed above. {511} facets are found to have similar effects on the growth and ordering of GaInP. Growth on deeply grooved substrates intentionally misoriented by 6° from (001) to produce [110] steps on the surface yields a single, highly-ordered (111) domain adjacent to disordered material produced by the formation of a (115) facet from the highly stepped region of the groove[34]. The growth rate of the (115) facet is much faster than for the other regions of the groove. The cross section of this structure was scanned using CL imaging. The CL peak from the ordered region was seen to occur at an energy 110 meV lower than the CL peak from the disordered region. Since the composition of the GaInP was found to vary little between these two areas, the difference in the peak energies is interpreted to be due to the lower band gap of the ordered material. This is the first direct demonstration of the effect of ordering on the energy band gap of GaInP[9].
CONCLUSIONS

The evidence presented in this paper suggests that surface reconstruction, the structure of [110] steps on the surface, and the motion of these steps on the surface determines the ordered structure formed during epitaxial growth as well as the degree of order. However, it would be premature to claim any detailed understanding of the complex processes occurring. Rather than summarizing the discussion, it is perhaps more useful to conclude this paper with a list of questions addressed to the theoreticians and the experimental specialists in the areas of surface physics and epitaxial growth:
1) Is ordering due to misorientation of the surface, the presence of steps, or step motion?
2) What is the atomic arrangement on the (001) surface during OMVPE growth of GaAs, GaInP, and other III/V compounds and alloys?
3) How is the surface reconstruction different for a {511}-oriented surface?
4) Does the absence of group V dimers on the {511} surface lead to the higher growth rate and disordered material?
5) What is the nature of [110] steps in GaAs grown by OMVPE and MBE? Does it change with changing V/III ratio?
6) Are atoms able to attach only at kink sites on [110] steps? Is this the reason for the long diffusion lengths observed?

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