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Long-range order in $(GaAs)_{1-x}Ge_{2x}$ and $(GaSb)_{1-x}Ge_{2x}$: Predictions for ⟨111⟩ growth

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We present an analysis of epitaxial growth of the pseudobinary alloys of the III-V semiconductor compounds GaAs and GaSb with the group IV semiconductor germanium. This work extends the growth model of Davis and Holloway from ⟨100⟩-oriented to ⟨111⟩-oriented growth, which has not yet been explored experimentally. We find that the direction of growth has a large influence on the long-range order in these alloys. Particularly we predict the following: (1) The order-disorder transition that is observed at about 30 mol % Ge in ⟨100⟩-grown alloys does not occur with ⟨111⟩ growth. Instead, some zinc-blende order is retained so long as any of the III-V component is present. (2) Growth in the ⟨111⟩Ga direction is unstable with a tendency for spontaneous conversion to ⟨111⟩As growth. (3) The short-range order is similar for both directions of growth. From this we infer that the energy gap of $(GaAs)_{1-x}Ge_{2x}$ will also be similar for ⟨111⟩-grown and ⟨100⟩-grown specimens.

I. INTRODUCTION

Metastable pseudobinary alloys of the III-V compound semiconductors GaAs and GaSb with the group IV semiconductor Ge have been made by Greene and coworkers,[1–4] using a modified sputtering technique. The alloys of Ge with GaAs have also been made by metalorganic chemical-vapor deposition[5] (MOCVD) and molecular-beam epitaxy[6] (MBE) methods. At present we lack a comprehensive physical characterization of these materials. We know the composition dependence of the optical energy gap[3] of $(GaAs)_{1-x}Ge_{2x}$, but little about its long-range zinc-blende ordering or about its atomic environments. In contrast, with $(GaSb)_{1-x}Ge_{2x}$ we have x-ray[7] and Raman[8,9] data related to the zinc-blende order and extended x-ray-absorption fine structure[10] (EXAFS) information about the nearest-neighbor (NN) environments, but we lack experimental information about its energy gap. Finally, we note that almost all of the information about these alloys relates to specimens that had been grown as epitaxial layers on ⟨100⟩-oriented substrates. [A few measurements have also been made on $(GaSb)_{1-x}Ge_{2x}$ grown on glass substrates.] As we shall show, this feature is remarkably significant.

Despite the limited data, these alloys have stimulated considerable interest and some controversy about the factors that influence their energy gaps and their long-range atomic ordering. An early attempt at a theory of these materials was made by Newman and Dow[11] (ND), with a later extension along similar lines by Koiller *et al.*[12] The main feature of this approach was the invocation of a cooperative ordering process (in response to a local minimum in the free energy) to account for a transition from zinc-blende to diamond symmetry that occurs with a critical mole fraction of Ge, $x_c \approx 0.3$. This transition was assumed to be associated with the minimum of a deeply bowed energy gap versus composition curve.

The ND theory has two major weaknesses. First, it has been unable to provide an estimate of the critical composition, x_c, at which the order-disorder transition occurs. This value is a parameter that must be input to the theory. Secondly, it ignores possible restrictions on wrong NN's and thereby gives rise to an alloy structure with large concentrations of Ga-Ga and As-As (or Sb-Sb) NN pairs. In the ND calculations of the energy gap the influence of these wrong NN pairs was overlooked because the virtual-crystal approximation (VCA) was made. This is incapable of handling strong alloy scattering and particularly missed the closing of the energy gap at midrange compositions that would arise from the concentration of As-As pairs that is implied by the ND model. A further, lesser defect of the ND model is that it treats the Ga and As components as unassociated atomic constituents. Evidence for the growth of alloys with a more-or-less stoichiometric GaAs component in the presence of a large excess of As suggests that the Ga and As atoms actually occur as NN pairs.

The deficiencies of the ND model were pointed out by Holloway and Davis[13] (HD), who proposed a simple statistical model for the alloy lattice that has since become known as the percolation model. The essential features of this model were the avoidance of energetically disfavored Ga-Ga and As-As NN pairs together with the incorporation of GaAs as Ga-As NN pairs. Calculations of the energy gap without the inaccuracies of the VCA showed that the experimental data could be accounted for quite well by the short-range order of the percolation model. Further, the influence of long-range order on the gap (as postulated by ND) was shown to be negligible from calculations on samples in which antisite disorder in Ge-rich alloys was eliminated without introducing wrong NN's. The absence of wrong NN's that was postulated in the percolation model was subsequently confirmed with $(GaSb)_{1-x}Ge_{2x}$ by EXAFS measurements.[10] However, the percolation model, which had no adjustable parameters, also predicted that $x_c \approx 0.75$. This was shown, by later x-ray measurements,[7] to be much too large a value. In fact, $x_c \approx 0.3$.

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A more accurate approach to the long-range order was made by Kim and Stern[14] (KS) with a computer simulation of growth in the ⟨100⟩ direction. Here appropriate NN restrictions were imposed to avoid the wrong Ga-Ga and As-As (or Sb-Sb) NN pairs and the order-disorder transition was correctly derived to be at $x_c \approx 0.3$ without the input of any adjustable parameters. Further, from an analysis of growth spherically outward from a central nucleus together with the results of EXAFS measurements of layers grown on glass substrates, Stern and coworkers[10,14] made the remarkably astute deduction that the composition dependence of the long-range order could depend upon the direction of growth. In some other respects the KS model was still inadequate for accurate description of the alloys. Thus, the absence of imposed pairing of Ga and As atoms (as in the percolation model) led to the requirement of identical fluxes and behavior of the arriving Ga and As atoms in order to achieve stoichiometry of the GaAs component. This is unrealistic because growth of $(GaAs)_{1-x}Ge_{2x}$ is usually effected in the presence of a large excess of As, which is much more volatile than Ga. In addition, difficulties were encountered in attempts to model growth in the ⟨111⟩ direction, where the Ge component tended to accumulate on alternate {111} planes.

A more realistic simulation of growth in the ⟨100⟩ direction was provided by the growth model of Davis and Holloway[15] (DH). This involved a Monte Carlo (MC) simulation of the growth process together with confirmation of the main features using analytic approximations. Here, as in the percolation and KS models wrong NN pairs (Ga-Ga and As-As or Sb-Sb) were prohibited. Also, as in the percolation model, the imposition of Ga-As NN pairing provided a mechanism for attainment of stoichiometry of the GaAs component under the usual condition of a large excess of As.

The growth model gave essentially the same short-range order as the earlier percolation model and thereby the same composition dependence of the energy gap (since we expect the electronic states to be dominated by the short-range order, as discussed at some length in DH). However, in distinction to the percolation model, it also gave the correct composition dependence of the long-range order of ⟨100⟩-grown alloys and thereby the correct composition for the order-disorder transitions.

In the present paper we extend the growth model to alloys that are grown in the ⟨111⟩ direction. Here there is currently a complete lack of experimental information, so that our theoretical results are predictions that await confirmation or disproof. We find that the short-range order is essentially unchanged from that of ⟨100⟩ growth and thus we do not expect significant differences in the energy gaps of samples grown along different crystallographic axes. However, the long-range order is quite different for the two growth directions. In particular, we predict that growth in the ⟨111⟩Ga direction is unstable, with a tendency for conversion to ⟨111⟩As growth. Also we find that some remnant of zinc blende order persists so long as any of the III-V component is present in the alloys. Such behavior is incompatible with thermodynamic theories of the type proposed by ND. Thus our results provide a definitive test for distinguishing between the thermodynamic and kinetic explanations of the order parameter in these alloys.

II. THE GROWTH MODEL

In this section we describe the application of our growth model for $(GaAs)_{1-x}Ge_{2x}$ and related alloys to growth in the ⟨111⟩ direction instead of the ⟨100⟩ direction described in DH. Although the end results of this process will turn out to be quite different from our earlier results for ⟨100⟩ growth, the physical assumptions that we make are identical to those used for that case. The only modifications to the previous calculations are minor changes to the growth algorithm to take account of the difference in geometric relationships between lattice sites on successive planes of the crystal. Thus our earlier description of the growth simulation[15] applies with the only significant difference being the omission of some minor variations that were previously found to be inconsequential for ⟨100⟩ growth.

The model's features may be recapitulated as follows. We postulate that the structure of the alloy is determined by a stochastic growth process in which, first, As (in one form or another) is always present in large enough excess to react with any free Ga on the surface and, secondly, the substrate temperature is high enough to reevaporate any unreacted As. These conditions appear to be consistent with published descriptions of the growth of $(GaAs)_{1-x}Ge_{2x}$. Moreover, to the extent that excess Sb is used at high enough growth temperatures, they may also apply to $(GaSb)_{1-x}Ge_{2x}$. For convenience, the following discussions refer specifically to Ga and As, but the arguments may also be applicable to other pairs of elements from groups III and V.

The conditions used for implementation of our model are those previously termed the "simple" implementation for ⟨100⟩ growth. They are described below. Since we will be considering layer-by-layer growth, it will be convenient to refer to the lattice plane whose vacant sites are being filled randomly by Ge or Ga atoms as the "current" plane. The corresponding about-to-be-filled and just-filled planes may then be referred to as the following and the preceding or underlying planes, respectively.

(i) Epitaxial growth is initiated on a {111} lattice plane of a GaAs substrate. This plane is populated with As atoms, corresponding to a pure GaAs substrate. However, the relationship of this plane to those that precede and follow it may correspond to growth in either a ⟨111⟩As or a ⟨111⟩Ga direction. (For clarification of the geometry, see Fig. 1.)

(ii) Layer-by-layer growth of the alloy is simulated by filling vacant sites on successive lattice planes with a random choice of either Ge or Ga atoms. Within each plane the vacant sites are filled in random sequence. When a Ga atom is added it reacts immediately with an As atom, which then occupies an NN site on the following plane. (This is the only mechanism for incorporation of As into the alloy.)

Published descriptions of $(GaAs)_{1-x}Ge_{2x}$ growth generally indicate the presence of a significant excess of As,

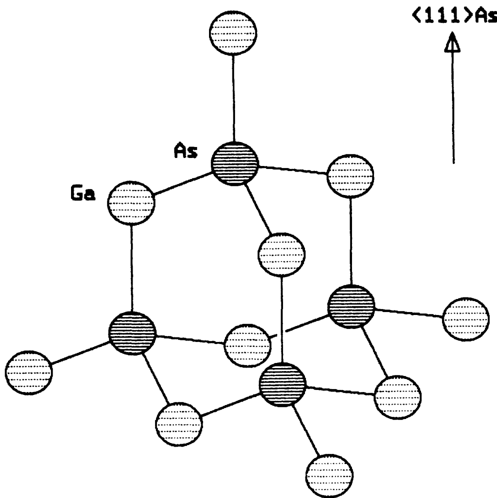


FIG. 1. Part of the GaAs lattice showing the alternation of Ga and As {111} layers. For the ⟨111⟩As direction the As atoms are triply bounded to the underlying layer.

of which only enough is incorporated to maintain approximate stoichiometry of the GaAs constituent. Our postulated addition of GaAs as molecules appears to be the simplest way to achieve this result. (Individual Ga and As atoms may dissolve in Ge to a much smaller extent, to act as acceptor and donor impurities, respectively.)

(iii) The addition of a Ga atom is subject to the condition that it does not create either a Ga-Ga or an As-As NN pair. (We note that Ga-Ga and As-As or Sb-Sb NN pairs are rare in pure GaAs and GaSb and that, from the evidence cited in Sec. I, the existence of significant concentrations of these wrong NN's in the alloys is unlikely.)

At each vacant site the decision to add a Ge atom is made definitely with a predetermined probability P_{Ge}. The alternative decision, to add a Ga atom (with an NN As atom on the following {111} plane) will then occur with the complementary probability $1-P_{Ge}$. However, in this case the decision is tentative and the Ga addition is only made after confirming that it will not give undesired NN pairs. If addition of a Ga-As atom pair would violate an NN restriction, the Ga atom reevaporates and a Ge atom is added instead.

(iv) The simulation created a succession of {111} lattice planes bounded by orthogonal {110} planes. For application of NN restrictions to atoms at the boundaries, we assumed that the sample was periodic across these {110} boundaries.

(v) From our experience with simulated ⟨100⟩ growth (described in Ref. 15) we chose not to explore with ⟨111⟩ growth the possible variations in which the NN restrictions were relaxed at phase-antiphase domain boundaries (which had given too large a concentration of As-As pairs) and in which Ga adatoms were allowed to move across the surface in search of suitable sites (because this had been found to have negligible influence on the results). We did try once more the effect of removing the periodic boundaries and found that their influence was insignificant, as it had been with ⟨100⟩ growth.

III. RESULTS OF MONTE CARLO SIMULATIONS

For our discussions of long-range order we define "phase" and "antiphase" orientations of the GaAs constituent of $(GaAs)_{1-x}Ge_{2x}$ to have their Ga and As atoms occupying different sets of alternate {111} planes. This then corresponds to a particular ⟨111⟩ direction being either ⟨111⟩As, as shown in Fig. 1, or ⟨111⟩Ga. (At this stage the assignment of phase or antiphase designations to either the ⟨111⟩As or ⟨111⟩Ga directions is arbitrary. We will later have reason to make a particular choice.) We may then define an antisite fraction, f, of the alloy to be the fraction of the GaAs constituent that is in the alternative "antiphase" orientation. Possible values of f range from zero, for the fully ordered zinc-blende lattice, to 0.5 for the completely disordered diamond lattice ($f=1.0$ for a fully ordered zinc-blende lattice with the antiphase orientation). The antisite fraction may be related to an order parameter M (defined equivalently to that of ND) by

$$M=(1-x)(1-2f) . \quad (1)$$

It is helpful to have a simple measure of the sizes of the continuous clusters or domains of Ge and GaAs (both phase and antiphase) that occur within a sample of the alloy. For this purpose we associate with each atom of the sample a length l that we define as the number of layers that may be reached from the atom by traveling to preceding layers via NN atoms of the same component, i.e., either Ge or one of the two orientations of GaAs. (From Fig. 1 we can see that each site on a {111} plane has either one or three NN's on the preceding plane.) For Ge atoms we will always travel back through the crystal via other Ge atoms, but for Ga or As atoms we will trace a path via alternate Ga and As atoms with opposite sequences for phase and antiphase domains. Our measure of the domain size in the growth direction is then the average of this length, $\langle l \rangle$, over all of the atoms of the appropriate type within the sample. Clearly, as a component's concentration becomes large enough $1/\langle l \rangle \rightarrow 0$, corresponding to a domain with infinite depth. The concentration at which this occurs resembles a percolation threshold for the growth direction. However, our clusters will be smaller than those usually considered in percolation theory because we do not count cluster members that might be reached by a combination of backward and forward moves through the sample. Thus, the onset of infinite domain depth for a component, as measured here, sets an upper bound to the concentration for a conventional percolation threshold. In fact, the restrictions to moves in one direction through the sample gives a situation akin to percolation on a tree, except that our lattice has more complexity than a tree because our paths may diverge and then rejoin at some underlying site. Nonetheless, our definition of $\langle l \rangle$ does give a useful and readily calculable measure of domain size. Particularly, the MC simulations are simplified and made capable of

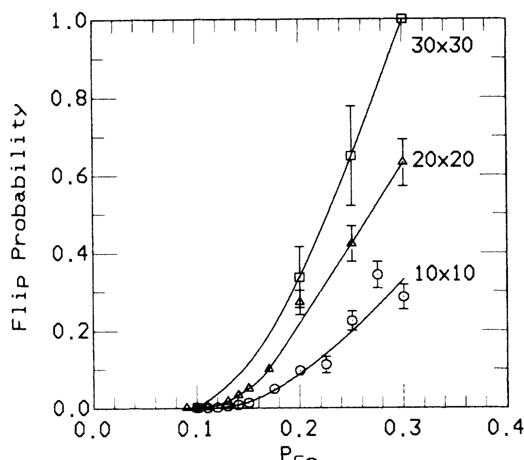


FIG. 2. Probability, as a function of P_{Ge}, that addition of a pair of {111} planes to the alloy growing in the ⟨111⟩Ga direction will cause nucleation of a stable domain with the ⟨111⟩As orientation and thereby flip the direction of growth. The three curves are for MC simulations with different sample sizes as shown and the error bars are one-σ limits.

extension to very large samples because we need to keep track of the occupancy of the sites on only three successive planes and of the values of l on only two planes.

Growth simulations were carried out using {111} planes that ranged from 10 by 10 to 30 by 30 atoms (along ⟨110⟩ directions orthogonal to the growth direction) with most of the work being done at 20 by 20 atoms. Very little dependence of the results upon the size of the cross section was found although, as might be expected, the smaller specimens gave larger fluctuations in the lattice statistics. To ensure attainment of a steady state, at least 1000 planes were grown before beginning the averaging of sample properties and in some cases even longer lead-ins were made. The averages were mostly of 2000 planes, although the properties of samples grown in the ⟨111⟩Ga direction were studied with up to 20000 planes.

From Fig. 1 we see that we need to consider ⟨111⟩ growth in two nonequivalent opposite directions, i.e., the ⟨111⟩As direction, as shown there, and the ⟨111⟩Ga direction. However, growth simulations showed that growth in the ⟨111⟩Ga direction was unstable with a tendency for spontaneous conversion to ⟨111⟩As growth as successive alloy layers were added. This tendency was observed with $P_{Ge} \gtrsim 0.1$ and, as shown in Fig. 2, the rapidity of the conversion to ⟨111⟩As growth increased with increase of the sample size in the range 10 by 10 to 30 by 30. Plane-by-plane inspection of MC simulated growth in the ⟨111⟩Ga direction at small values of P_{Ge} showed that, in the early stages, the population of our sample planes was dominated by a domain with the ⟨111⟩Ga orientation. This could persist for several thousand planes when $P_{Ge} \approx 0.1$ and for shorter distances for larger P_{Ge}. However, from time to time small domains with the ⟨111⟩As orientation would appear. These might disappear after a few tens of planes, but eventually one would persist and take over most of the GaAs content of the sample planes (in fact, at small P_{Ge} all of the Ga and As atoms with large values of l). The opposite phenomenon, of conversion from ⟨111⟩As to ⟨111⟩Ga growth, was never observed in our simulations.

These results suggest that the conversion to ⟨111⟩As growth depends upon initiation of a stable ⟨111⟩As domain with a probability that increases with the area of the sample planes. If so, the phenomenon is to be expected at much smaller Ge contents in macroscopic specimens. Such behavior might be related to observations of preferred ⟨111⟩As growth in heteroepitaxy of GaAs on Ge.[16]

From this point onward we will consider only growth of the alloys in the stable ⟨111⟩As direction. In recognition of the preference for growth in this direction we will define the phase orientation of the GaAs component to be that with its Ga and As atoms on the appropriate {111} planes for ⟨111⟩As growth and the antiphase orientation to be that with site occupancies corresponding to ⟨111⟩Ga growth.

Figure 3 shows the composition dependences of $1/\langle l \rangle$ for the Ge component and the phase and antiphase GaAs components that we obtained from MC simulations. These results subdivide the composition range into three regions as follows.

(1) When Ge is added to GaAs we first pass through a range ($x \lesssim 0.36$) where the alloy has an infinite domain of the GaAs phase component. With increasing Ge content the antiphase GaAs component increases its concentration and its domains, though finite, have increasing average length. In this region the Ge domains are also finite.

(2) Next we find a region ($0.36 \lesssim x \lesssim 0.61$) where the domains of all three components are finite. In this region

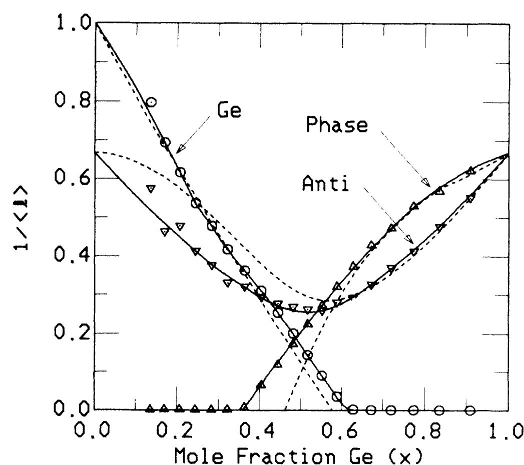


FIG. 3. Composition dependence of the reciprocal of the mean cluster length ($1/\langle l \rangle$). The symbols joined by solid lines are the MC results for Ge (circles), phase GaAs (triangles with vertices up), and antiphase GaAs (triangles with vertices down). (Here phase is defined relative to the ⟨111⟩As direction.) The dotted lines are the analytic approximations for these quantities.

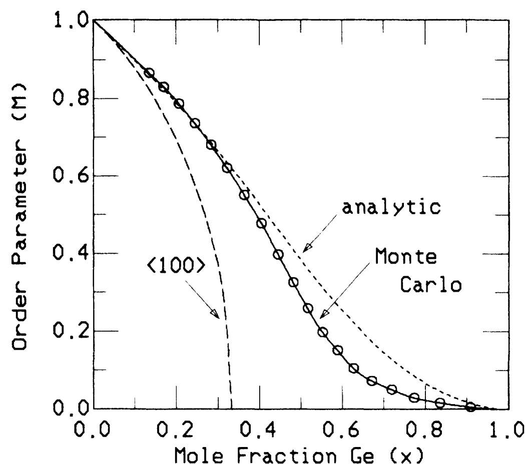


FIG. 4. Composition dependence of the order parameter. The circles connected by a solid line are the MC results and the dotted line is the analytic approximation for ⟨111⟩ growth. The dashed line shows the corresponding analytic approximation for ⟨100⟩ growth. (The latter is in good agreement with both MC and experimental results.)

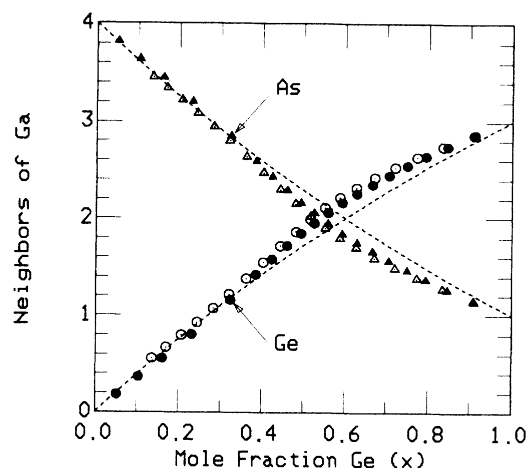


FIG. 6. Composition dependence of the environment of a Ga atom. The open and solid symbols are the MC results for ⟨111⟩ and ⟨100⟩ growth, respectively, and the dotted lines are the analytic approximations for the number of NN's. Note that the NN environment of an As atom is identical to this except that As NN's are replaced by Ga NN's.

the antiphase clusters attain their maximum extent with $\langle l \rangle \approx 4$.

(3) Finally, with $x \gtrsim 0.61$, the domains of both GaAs orientations remain finite, but the Ge component acquires an infinite domain.

Figure 4 shows the composition dependence of the order parameter calculated for ⟨111⟩ growth, together with the corresponding result for ⟨100⟩ growth. The results for the two growth directions are strikingly different, with the ⟨111⟩ direction lacking a transition from zinc-blende to diamond symmetry. These results are discussed further in Sec. IV, as are the MC results for the average NN environments of Ge and Ga that are shown in Figs. 5 and 6.

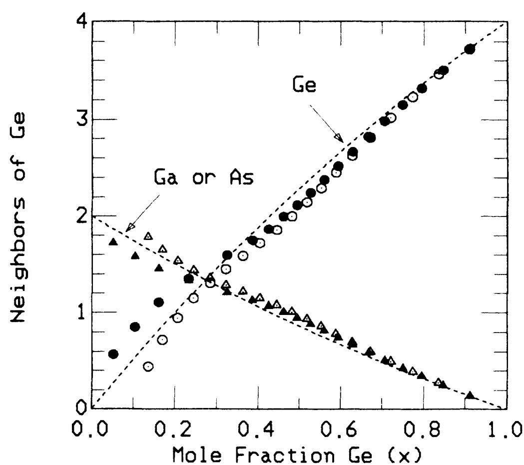


FIG. 5. Composition dependence of the environment of a Ge atom. The open and solid symbols are the MC results for ⟨111⟩ and ⟨100⟩ growth, respectively, and the dotted lines are the analytic approximations for the number of NN's. Note that both the analytic approximation and the MC results are identical for Ga and As NN's.

IV. ANALYTIC APPROXIMATIONS

Analytic approximations for the order parameter, the domain lengths, and the NN environments may be derived by approaches similar to that taken for ⟨100⟩ growth in Ref. 15. As in that work, the analytic approximations sacrifice some accuracy relative to the MC simulation, but confirm its major results and give insight into their origins.

Inspection of Fig. 1 shows that the {111} planes of the zinc-blende lattice alternate between two kinds. These are bonded to, respectively, one and three NN's in the underlying {111} plane. In the example shown, with pure GaAs, growth in a ⟨111⟩As direction gives As atoms that are triply bonded and Ga atoms that are singly bonded to their underlying layers. These relationships are interchanged for growth in a ⟨111⟩Ga direction. For the alloys with Ge we may define for the nth {111} plane the probabilities $p_1(n)$ and $p_3(n)$ that a site is occupied by a Ga atom. Here p_1 applies when the site is singly bonded to the underlying {111} plane and p_3 applies when it is triply bonded (i.e., each of these probabilities is only defined for alternate {111} planes). We may now follow DH by expressing the probability that a site on a particular plane becomes occupied by Ga in terms of the probability that none of its underlying NN sites contains a Ga atom. This leads to

$$p_3(n+2)=(1-P_{Ge})[1-p_1(n+1)]^3 \quad (2a)$$

and

$$p_1(n+1)=(1-P_{Ge})[1-p_3(n)] \ . \quad (2b)$$

As in DH we have neglected both the in-plane correlations of site occupancy (corresponding to second NN relationships) and the NN restrictions on the companion As atom. We note that this alternation of the relationships between the values of p for successive layers differs from the single relationship that was derived for ⟨100⟩ growth by DH

$$p(n+1)=(1-P_{Ge})[1-p(n)]^2 \ . \quad (3)$$

This difference arises because, with ⟨100⟩ growth, the sites in all planes have two underlying NN sites.

We now look for steady-state solutions of Eqs. (2), i.e., for solutions with

$$p_1(n+1)=p_1(n+3)=\cdots=p_1 \quad (4a)$$

and

$$p_3(n)=p_3(n+2)=\cdots=p_3 \ , \quad (4b)$$

where p_1 and p_3 are the steady-state values. Elimination between Eqs. (2) then leads to a pair of cubic equations for p_1 and p_3. These are not particularly transparent, but for the region of interest, with $0<P_{Ge}<1$, each has three real roots of which only one satisfies the condition for physical reality that $0\le p_1, p_3\le 1$. This corresponds to the relatively simple expression

$$P_{Ge}=1-[1-(1-4p_1\{1-p_1\}^3)^{1/2}]/2(1-p_1)^3 \ . \quad (5)$$

The solutions with physical significance are shown in Fig. 7. (At $x=0$, i.e., for pure GaAs, we acquire a second solution with physical significance and we may have either $p_1=1$ and $p_3=0$, corresponding to ⟨111⟩As growth or $p_1=0$ and $p_3=1$, corresponding to ⟨111⟩Ga growth.)

From Fig. 7 it is immediately evident that the steady-state solution gives a preponderance of Ga atoms on sites that are singly bonded to the underlying {111} plane, i.e., that steady-state growth of the alloy corresponds to a ⟨111⟩As direction. This confirms our MC result. The order parameter may be defined equivalently to Eq. (1) by

$$M=p_1-p_3 \ , \quad (6)$$

from which, together with the solutions in Fig. 7, it is clear that the order parameter only becomes zero when $P_{Ge}=1$, otherwise some remnant of zinc-blende order persists so long as any of the GaAs component is present. This is also in accord with the MC simulations of ⟨111⟩ growth and, as shown in Fig. 4, the two approaches are in fair agreement for the composition dependence of the order parameter.

We may note that for a non-steady-state value

$$p_1(n+1)=p_1+\delta_{n+1} \ , \quad (7)$$

with $\delta_{n+1} \ll p_1$, we will obtain

$$p_1(n+3)=p_1+\delta_{n+3} \ , \quad (8)$$

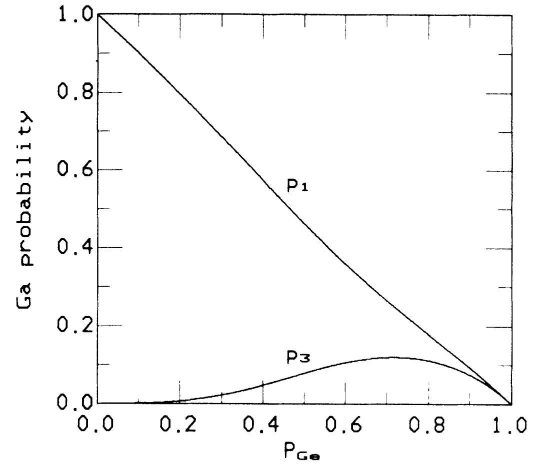


FIG. 7. Composition dependence of the solutions p_1 and p_3 for the steady-state Ga concentration in {111} layers that are, respectively, singly and triply bonded to the underlying {111} layer. These solutions correspond to ⟨111⟩As and ⟨111⟩Ga growth, respectively.

where the ratio

$$\delta_{n+3}/\delta_{n+1}=3(1-P_{Ge})^2(1-p_1)^2 \quad (9)$$

must be less than unity for stability of the solution. Examination of the values shows that this is the case for $0<P_{Ge}<1$. (The same ratio also provides a criterion for the stability of p_3.) The development of p_1 and p_3 for successive layers of the alloy is shown in Fig. 8. Here we have started at layer 1 with $p_1=0$, corresponding to a complete antiphase (i.e., ⟨111⟩Ga) orientation. Using a moderately small value of $P_{Ge}=0.05$ we find that p_1 and

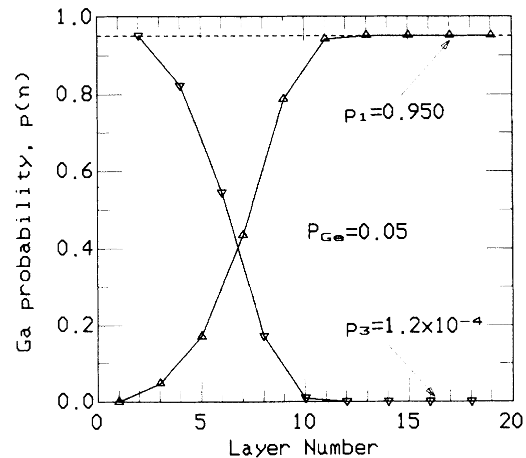


FIG. 8. Development of the values of the Ga probabilities p_1 and p_3 with addition of layers to a sample that starts with GaAs in the antiphase orientation. The probability for Ge substitution is $P_{Ge}=0.05$.

p_3 attain their steady-state values corresponding to a predominantly ⟨111⟩As orientation after the addition of only about ten layers. (Larger values of P_{Ge} give more rapid approaches to steady state.) This flip from ⟨111⟩Ga to ⟨111⟩As growth accords with that observed in the MC simulations, although it occurs here much more rapidly. This lends support to our suggestion that the transition in the MC simulations was hindered by the small areas of the sample layers.

We now derive analytic approximations to the domain length, $\langle l \rangle$. These follow DH by replacing the actual lattice with a tree. This will be appropriate for modeling the cluster length that is obtained from the MC simulations because it likewise corresponds to a unidirectional progress from node to node. We approximate the lattice by a tree with nodes that undergo threefold branching at every second {111} layer. Thus the potential members of a cluster will be assumed to increase as 1,3,9,27,... as we reach successive second layers. Inspection of Fig. 1 shows that the potential membership actually increases more slowly, i.e., as 1,3,6,10,... because underlying sites may be reached by alternative routes. This has the effect that the number of cluster members will be overestimated at large concentrations of a constituent. However, our cluster undergoes branching and becomes infinite in extent as soon as the number of members expected on underlying layers exceeds unity. Thus, our approximation will be reasonable for finite clusters.

We note that for a tree with q-fold branching at each node together with a concentration x of a monatomic substituent, the number of like NN's expected as we proceed from a particular site is $r = qx$. Consistency then requires that, for small r, we have

$$\langle l \rangle = 1 + r \langle l \rangle = 1/(1-r) , \tag{10}$$

which gives $\langle l \rangle \to \infty$ when $r = 1$. This is exactly the condition for the percolation threshold of a tree.[17] Our derivations for the cluster lengths of the alloy constituents follow an approach that is similar to this simple example, but with the added complication of a different geometry for alternate layers and of a pairing of Ga and As atoms.

Consider first the Ge constituent. We will assume that the probability of finding a site occupied by a Ge atom is just the mole fraction x. If we define $\langle l \rangle_1$ to be the value of the cluster length when we start at a Ge atom that is singly bonded to the underlying layer, consistency requires that

$$\langle l \rangle_1 = 1 + x + 3x^2 \langle l \rangle_1 = (1+x)/(1-3x^2) \tag{11}$$

when $x \ll 1$. Similarly, for a start at a Ge atom that is triply bonded to the underlying layer

$$\langle l \rangle_3 = 1 + 3x \langle l \rangle_1 , \tag{12}$$

again for small x. Thus, averaging we obtain

$$\begin{aligned}\langle l \rangle_{Ge} &= (\langle l \rangle_1 + \langle l \rangle_3)/2 \\ &= \tfrac{1}{2} + (1+x)(1+3x)/2(1-3x^2) .\end{aligned} \tag{13}$$

This gives an infinite length when $x = 0.577$, which is in reasonable accord with the value, $x = 0.61$, obtained from the MC simulations. As shown by the dotted line in Fig. 3, the composition dependence of finite $\langle l \rangle_{Ge}$ is also in good agreement with the MC results

We consider next the lengths of clusters with the phase orientation for ⟨111⟩As growth. If we start with an As atom this will be triply bonded to the underlying layer. Of the three underlying NN's, one must be a Ga atom from the pairing imposed during growth. The other two underlying sites will be occupied by Ga atoms with probability

$$s_1 \approx p_1/(1-p_3) = 1 - P_{Ge} , \tag{14}$$

since know that neither of these sites can contain an As atom. Similarly, the site under a Ga atom will be occupied by an As atom with probability s_1. Consistency then requires that for small s_1 the expected length starting at an As atom is

$$\langle l \rangle_{As} = 2 + s_1(1+2s_1)\langle l \rangle_{As} = 2/(1-s_1-2s_1^2) . \tag{15}$$

Also, starting at a Ga atom we have

$$\langle l \rangle_{Ga} = 1 + s_1 \langle l \rangle_{As} , \tag{16}$$

whence averaging gives

$$\begin{aligned}\langle l \rangle_{phase} &= (\langle l \rangle_{As} + \langle l \rangle_{Ga})/2 \\ &= \tfrac{1}{2} + (1+s_1)/(1-s_1-2s_1^2) .\end{aligned} \tag{17}$$

This gives an infinite cluster when $s_1 = 0.5$, corresponding to $x = 0.46$.

Comparison of the calculated $1/\langle l \rangle_{phase}$ with that obtained from MC simulations in Fig. 3 shows that we have somewhat overestimated the mole fraction of Ge above which the phase cluster length ceases to be infinite, obtaining $x = 0.46$ instead of 0.36. However, the agreement between the two values of $\langle l \rangle$ is remarkably good at smaller GaAs contents (i.e., for $x \gtrsim 0.65$).

We now consider the lengths of clusters with the antiphase orientation relative to ⟨111⟩As growth. In this case the As atoms occupy the sites that are singly bonded to the underlying lattice and our approximations for small concentration are

$$\langle l \rangle_{As} = 2 + 3s_3 \langle l \rangle_{As} = 2/(1-3s_3) \tag{18}$$

and

$$\langle l \rangle_{Ga} = 1 + 3s_3 \langle l \rangle_{As} , \tag{19}$$

where

$$s_3 = p_3/(1-p_1) = (1-P_{Ge})(1-p_1)^2 . \tag{20}$$

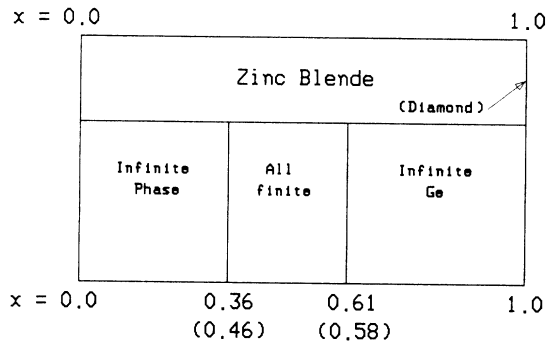
Averaging as before gives

$$\begin{aligned}\langle l \rangle_{anti} &= (\langle l \rangle_{As} + \langle l \rangle_{Ga})/2 \\ &= \tfrac{1}{2} + (1+3s_3)/(1-3s_3) .\end{aligned} \tag{21}$$

For an infinite antiphase cluster we would then require that $s_3 \geq 0.333$, which condition is not reached in the composition range $0 < x < 1$. Inspection of Fig. 3 shows that the analytic approximation reproduces well the qualitative behavior of the MC simulation over the whole of

the composition range and it also gives remarkably good quantitative agreement at smaller GaAs contents (i.e., for $x \gtrsim 0.6$).

Our analytic approximations confirm the overall results of the MC simulations of ⟨111⟩ growth and they reinforce our prediction of behavior that is significantly different from that previously observed and explained for ⟨100⟩ growth. A comparison of the two cases is given in Fig. 9. Here Fig. 9(b), for ⟨100⟩ growth, is from the previous analysis in Ref. 15. We note first, and most obviously, that the ⟨111⟩-grown alloys are predicted to retain some zinc-blende long-range order for all compositions except that of pure Ge, i.e., $x_c = 1$. This is in sharp contrast to the ⟨100⟩-growth alloys, where experimental data, MC simulations, and analytic approximations all give a transition from zinc-blende to diamond symmetry when $x = x_c \approx 0.3$. The other major difference is that the ⟨100⟩-grown alloys are predicted to have a regime in which infinitely long phase and antiphase GaAs domains coexist. This region is missing in the predicted behavior of ⟨111⟩-grown alloys, where the antiphase (⟨111⟩Ga) orientation never attains infinite cluster length.



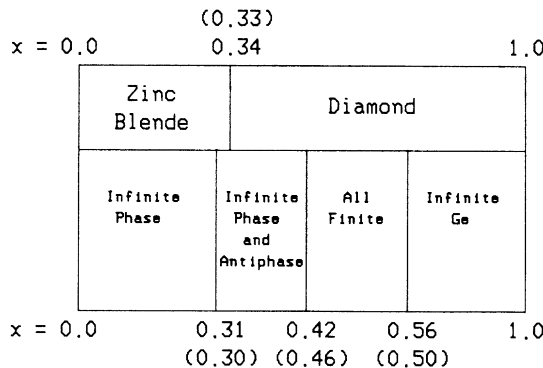


FIG. 9. Composition dependences of the properties of $(GaAs)_{1-x}Ge_{2x}$ and $(GaSb)_{1-x}Ge_{2x}$ for growth in (a) the ⟨111⟩ and (b) the ⟨100⟩ direction. The mole fractions of Ge in parentheses are from the analytic approximations and the unparenthesized values are from the MC simulations. Here the designations of infinite domains refer to the value of $\langle l \rangle$, rather than to the size of a conventionally percolating cluster.

Finally we consider analytic approximations to the NN environments. Here we may apply the approximations that were derived by DH without modification since these did not involve any assumptions about the growth direction. Thus, denoting the average number of neighbors of type j around an atom of type i by $N_{i,j}$ we have (as derived by DH)

$$N_{\mathrm{Ga,Ge}} = 12x/(x+3) , \tag{22}$$

$$N_{\mathrm{Ge,Ge}} = 16x/(x+3) , \tag{23}$$

$$N_{\mathrm{Ga,As}} = 4(3-2x)/(x+3) , \tag{24}$$

and

$$N_{\mathrm{Ge,As}} = 6(1-x)/(x+3) , \tag{25}$$

where the remaining quantities of interest follow from symmetry, e.g., that $N_{\mathrm{As,Ge}} = N_{\mathrm{Ga,Ge}}$, and from the requirement that each atom has four NN's.

Comparison of the analytic approximations for the average NN environments of Ge and Ga with the MC results is given in Figs. 5 and 6. In both cases the agreement between the analytic and the MC results is good and there is also excellent agreement with MC data for ⟨100⟩ growth, as might be expected from the direction independence of the analytic approximations. (The largest difference between the MC results for the two directions is in the environment of Ge at small x. This is the region in which we have shown that the finite size of our sample planes can influence the MC results.[18]) Our MC results gave an NN environment of an As atom that was identical to that shown here for a Ga atom except for interchange of the roles of As and Ga.

V. SUMMARY AND CONCLUSIONS

We have extended our growth model for the alloys $(GaAs)_{1-x}Ge_{2x}$ and $(GaSb)_{1-x}Ge_{2x}$ from ⟨100⟩ growth to ⟨111⟩ growth. By so doing we have progressed from explanations of known behavior to predictions about a regime that has not yet been explored experimentally. The predictions include some substantial differences from the results that have been reported previously for ⟨100⟩ growth, particularly with respect to the long-range order, and are as follows.

(1) We predict that ⟨111⟩-grown layers will not exhibit the zinc blende to diamond transition that has been observed at $x_c \approx 0.3$ with ⟨100⟩-grown layers. Instead, there will be some remnant of zinc-blende order at all compositions, except that of pure Ge (i.e., $x_c = 1$).

(2) We predict that growth in the ⟨111⟩Ga direction is unstable, with a tendency for conversion to ⟨111⟩As growth as the layer thickness increases.

(3) We predict that the short-range order will be identical to that obtained with ⟨100⟩ growth. Since our previous work has shown that the energy gap of $(GaAs)_{1-x}Ge_{2x}$ is dominated by the short-range order we therefore also predict an energy gap for this alloy that is almost identical to that of ⟨100⟩-grown material, despite

the substantial difference in long-range order with ⟨111⟩ growth. [For example, with our percolation model (HD) we found that the gap of ⟨100⟩-grown material was not significantly affected by elimination of site-antisite disorder, provided that we did not thereby create wrong NN pairs. Further, the major change in long-range order of ⟨100⟩-grown layers on going from the percolation model to the growth model (DH) had similarly negligible effect.]

At this stage we await an experimental test of our predictions. However, it seems appropriate to state briefly the conclusions that will follow if they are verified.

If our prediction of a different composition dependence of the order parameter with ⟨111⟩ growth is confirmed, explanations of the zinc blende to diamond transition, such as that proposed by ND, in terms of a local minimum in the free energy of the crystal structure will become quite untenable. Clearly, a dependence of the order upon the growth direction would require the intervention of kinetics, rather than of quasiequilibrium thermodynamics. (From the discussion in Sec. I it is evident that the ND model must already be regarded as unsatisfactory for other reasons.)

If ⟨111⟩-grown specimens fulfill both the prediction of a different long-range order and that of a similar energy gap to ⟨100⟩-grown specimens, we will be able finally to discount the ND postulate that the minimum in the energy gap is related in some way to the occurrence of an order-disorder transition. (From the discussion in Sec. I, and from the arguments of DH, there is already a strong case that the occurrence of the minimum gap and the order-disorder transition at about the same composition in ⟨100⟩-grown alloys is coincidental.)

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[18]The algorithms for simulation of ⟨100⟩ and ⟨111⟩ growth might be expected to give slightly different behavior at small x for two reasons. First, the finite-size effect (discussed for ⟨100⟩ growth in Ref. 15) should be smaller with ⟨111⟩ growth. The NN pairing of Ga and As atoms has the secondary effect that Ge atoms are also added in pairs to adjoining layers, although these Ge pairs will only be NN's by coincidence. In the ⟨100⟩ case the two Ge atoms will occur not only in adjacent layers, but also in adjacent rows along a ⟨110⟩ direction in the {100} planes. At small x and with an N by N sample this then gives a probability of $2/N$ that a Ge atom will have a Ge NN. In contast, with the different geometry for ⟨111⟩ growth the two Ge atoms may occupy any pair of sites on consecutive {111} planes. This reduces the probability of fortuitous pairing to $3/N^2$ at small x. A second effect may arise from a minor simplification that was made to the algorithm for ⟨111⟩ growth. With ⟨100⟩ growth we had taken pains to avoid a potential "parking" problem that could occur with Ga-As pairing at small x. This could arise if the potential and suitable sites for the As atom of a Ga-As NN pair had been preempted by the choices of As NN's for adjacent Ga atoms. This problem was avoided with ⟨100⟩ growth by allowing placement of the As atom (subject to the usual NN restrictions) at the boundary of the GaAs domain, followed by rearrangement of the arbitrary grouping of Ga and As atoms into NN pairs. With this approach we were able to simulate the growth of pure GaAs in the ⟨100⟩ direction, without any forced addition of Ge atoms that would be imposed by inability to add Ga-As pairs. For the simulations of ⟨111⟩ growth we omitted this refinement as unnecessary for studies that were mostly aimed at elucidation of the effects of larger Ge concentrations.