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Model for the metastable system of type $(GaAs)_{1-x}(Ge_2)_x$

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A model is presented to explain the observed properties of the metastable alloy system of type $(GaAs)_{1-x}(Ge_2)_x$. It assumes only the observed short-range order and exhibits the critical composition x_c below which long-range order exists. The value of x_c in the model depends on the morphology of the kinetic growth. An analytic approximation is used to show the existence of x_c, the critical behavior of the correlation length, and the variation of the long-range order parameter S as a function of x.

I. INTRODUCTION

Metastable compounds of the form $(GaAs)_{1-x}(Ge_2)_x$ have been studied both experimentally and theoretically. Some examples are $(GaAs)_{1-x}(Ge_2)_x$,[1–5] $(GaAs)_{1-x}(Si_2)_x$,[6] $(GaSb)_{1-x}(Ge_2)_x$,[7,8] and $(GaSb)_{1-x}(Sn_2)_x$.[9] For the compound $(GaSb)_{1-x}(Ge_2)_x$, it has been found that there are no Ga-Ga or Sb-Sb nearest-neighbor pairs.[8] These compounds crystallize in a diamond-type lattice. At the low-x end the crystal has a long-range zinc-blende order as occurs for the $x=0$ compound, while at the high-x end the zinc-blende order disappears and only the diamond-lattice order remains as occurs at $x=1$. The disappearance of the zinc-blende order occurs at a critical composition x_c. The unusual feature of the transition is that x_c is not unique but varies with the morphology of the kinetic growth. Before the experimental result of the nonuniqueness of x_c was known, several theoretical models were proposed to explain the variation of the optical energy gap of these compounds as a function of x.[2–4] However, these models have to be supplemented to explain the variation of x_c. Since the alloys are metastable their properties are not thermodynamically controlled and their nonunique nature indicates that variations in the morphology of the kinetic growth process can affect their properties. In the literature a description of a possible transition of this type is known as a "kinetic" phase transition.[10–12] The model we proposed previously[8] and discuss in more detail here is different from the one described in Ref. 10, but it belongs to the same group in the sense that the transition depends on the kinetics of the growth, not on thermodynamics.

In this paper we describe our model in greater detail and discuss the predicted properties that are amenable to experimental verification. A spherical growth is used to model the sputtering of the samples onto a glass substrate. A planar growth is used to model the epitaxial growth onto a GaAs single-crystal (100) surface. The effect of varying the substrate for this (100) growth case is also investigated. A planar growth in the [111] direction has been studied to see if there is any variation when a different surface is used as the substrate.

We point out that the planar growth in the [100] direction is an extended form of the cellular automata problem.[13] It is different from the simple cellular automata problem described by Wolfram[13] in two aspects: ours is a three-state, not a two-state problem; and ours involves a probability while the simple one is totally deterministic. Nevertheless, the results show many of the characteristics of a cellular automata problem.

II. MODELS

Our model of growth occupies the sites of a diamond lattice in the following manner. The growth begins with an initial layer. Subsequent layers are added, one after the other. The first of the rules based on extended x-ray absorption fine structure measurements[8] is that no Ga-Ga or As-As nearest-neighbor pairs are allowed and no site is left vacant. (From now on, Ga, As, and Ge will be used as representatives of elements of groups III, V, and IV, respectively.) A parameter t determines the probability of having a specific atom at a given site. When there is no restriction, the probabilities of having Ge, Ga, and As at one particular site are t, $(1-t)/2$, and $(1-t)/2$, respectively. To satisfy the first rule, the probabilities are changed when the nearest-neighbor sites are already occupied by either Ga or As atoms. When both Ga and As occupy the nearest-neighbor sites, the site is forced to have a Ge atom. When there are only Ga and any Ge, the site is occupied by an As atom with the probability $(1-t)/(1+t)$ and Ge with $2t/(1+t)$; when there are only As and any Ge, the site is occupied by a Ga atom, with the same probabilities. The composition x is determined by counting the numbers of Ga, As, and Ge atoms after the growth is completed. Physically the model corresponds to crystal growth from a vapor, with probabilities of hitting a particular site given by the first probabilities. The probability of sticking depends on the nearest-neighbor environment. It is zero for Ga if there is a first neighbor of Ga (and zero for As if there is a first neighbor of As), while it is one for all other cases. This short-range-order restriction changes the probabilities to the second values given above.

In the case in which some of the elements are more volatile, e.g., As, so that the sticking coefficient may not reach one, the model is still applicable. In that case the first probabilities represent the product of the probability of hitting a particular site times the sticking coefficient.

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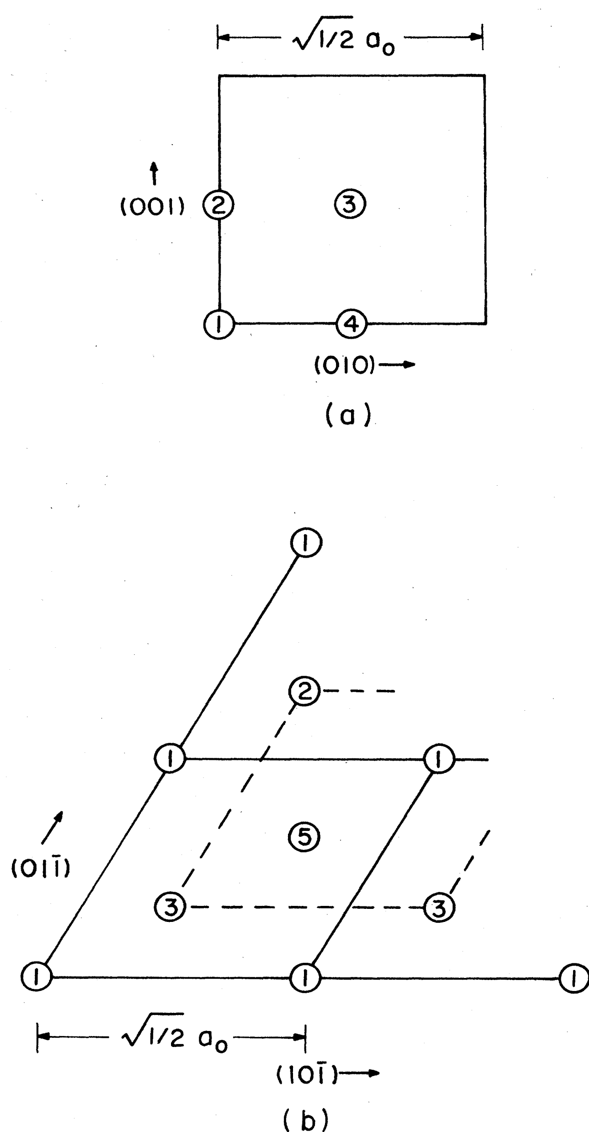

FIG. 1. Relative positions of sites in (a) the (100) planes and (b) the (111) planes of a diamond lattice. The conventional cubic lattice constant a_0 is the unit of distance in all figures.

Thus, an overpressure in the vapor would be required to compensate for a smaller sticking coefficient.

Some details are different from case to case. They are described below.

A. Planar growth in [100] direction

The initial and subsequent layers are (100) planes. The distance between neighboring planes is $\frac{1}{4}a_0$ (the lattice constant of a conventional cubic cell). The sites in the (100) plane form a square lattice whose unit cell size is $(\sqrt{2}/2)a_0$. The relative positions of sites in different layers are shown in Fig. 1(a). They repeat the pattern after four layers. There are always two already occupied nearest-neighbor sites, unless the site is on the edge of the plane. When a periodic boundary condition is applied, the above condition is true for every site. A periodic boundary condition was used for this study, except when stated explicitly otherwise.

All the sites in a layer belong to the same zinc-blende sublattice, and neighboring layers always belong to different ones. The initial plane is filled with Ga atoms to model the growth on a perfect GaAs (100) surface. Different initial planes were also used to see their effect on the growth.

B. Planar growth in [111] direction

The initial and subsequent layers are (111) planes. There are two different distances between neighboring planes, $(\sqrt{3}/4)a_0$ and $(\sqrt{3}/12)a_0$. The sites in a (111) plane form a triangular lattice whose lattice constant is $(\sqrt{2}/2)a_0$. When the next plane is separated from the preceding one by a distance of $(\sqrt{3}/4)a_0$, the sites are exactly on the top of sites in the preceding layer and each site has only one already occupied nearest-neighbor site just beneath it. When the next plane is $(\sqrt{3}/12)a_0$ from the preceding layer, each site has three already occupied nearest-neighbor sites, and the relative position of the sites in the new plane is as shown in Fig. 1(b). In Fig. 1(b), sites in planes 2, 4, and 6 are exactly on top of the sites in planes 1, 3, and 5, respectively. The pattern repeats after six planes.

As in the case of (100) planes, all the sites in one layer belong to the same zinc-blende sublattice and neighboring layers belong to different sublattices. As there can be two different initial planes, both cases were tested. (This is equivalent to saying that the crystal grows in the opposite direction.) Different conditions for the initial planes were used as in the [100] direction.

C. Spherical growth

The initial "layer" is one central atom, which in our study is Ga. A subsequent layer consists of sites equidistant from the central site. Other layers are added one by one in the order of increasing radius. There is no nearest-neighbor pair among sites in the same layer, and all the sites in one layer belong to the same sublattice of the zinc-blende structure. Each site has one, two, or three already occupied nearest-neighbor neighbor sites, depending on the geometry of the particular site and on the layer. Sites in the same layer do not necessarily have the same number of occupied nearest neighbors. Neighboring layers belong to different sublattices most of the time, but not always.

III. RESULTS OF COMPUTER SIMULATION

A. Planar growth in the [100] direction

First, we grew the crystal in the [100] direction with Ga filling all the sites of the initial plane. This corresponds

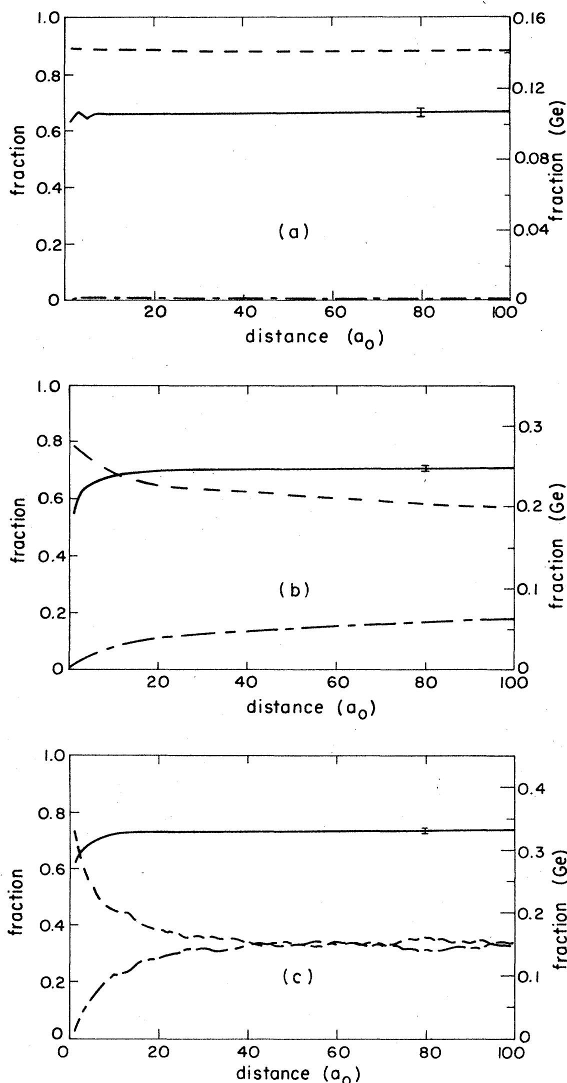

FIG. 2. The fractions of "right" (dashed line) and "wrong" (dashed-dotted line) atoms in a crystal grown in the [100] direction, as functions of the distance from the initial plane. Also plotted by the solid line is the fraction of Ge atoms: (a) $t=0.05$, $x=0.11$; (b) $t=0.10$, $x=0.25$; and (c) $t=0.14$, $x=0.33$. Fluctuations have been smoothed out, and the fluctuation is shown by error bars except when two curves are overlapping.

to a completely ordered initial state and simulates the actual growth on a GaAs single-crystal substrate. The cross section of the plane had dimensions of 100×100 primitive cells. A periodic boundary condition was applied. (To make sure that the plane was big enough, a few simulations were done on a plane of 150×150 primitive cells. The results were basically the same.) As the crystal grew, the number of "right" and "wrong" atoms were counted and their fractions were plotted as functions of the distance from the initial plane. In all even-numbered planes (including 0, the initial one), Ga are the "right" and As are the "wrong" atoms; the reverse is true in the odd-numbered planes. The results are shown in Fig. 2 for three different t (and consequently x) values as a function of film thickness. The decay length to attain the steady state becomes very large near x_c and decreases on either side.

When a steady state is reached, the order parameter can be determined. The order parameter S is defined as[14]

$$S=2\left[f-\frac{1-x}{2}\right],$$

where f is the fraction of Ga atoms in a Ga sublattice. When the order is perfect, $S=1-x$, while $S=0$ for a completely random system. The definition of the order parameter is equivalent to the difference between fractions of right and wrong atoms. The order parameter as obtained by the computer simulation as a function of x in the steady-state condition is given in Fig. 3. The uncertainties come from the fluctuations due to the finite number of atoms. The critical composition x_c, above which the order parameter becomes zero, is about $0.26^{+0.03}_{-0.02}$.

Next, we grew the crystal in the same direction but with different initial planes. Several initial conditions were used, but here we present only the results from the most disordered initial condition. All the sites in the initial plane were filled with Ge, giving a zero initial order parameter. Then the crystals were grown following the same rules. As there is no long-range order with $x>x_c$, even when the initial order parameter is one, we used only x values smaller than x_c. As there is no distinction between right and wrong atoms, one was arbitrarily chosen as the right atom and the other as the wrong one.

The order parameter of the crystal grown from the disordered initial plane is not as large as the one grown from an ordered initial plane, even after allowing further growth. But when the final plane is examined carefully,

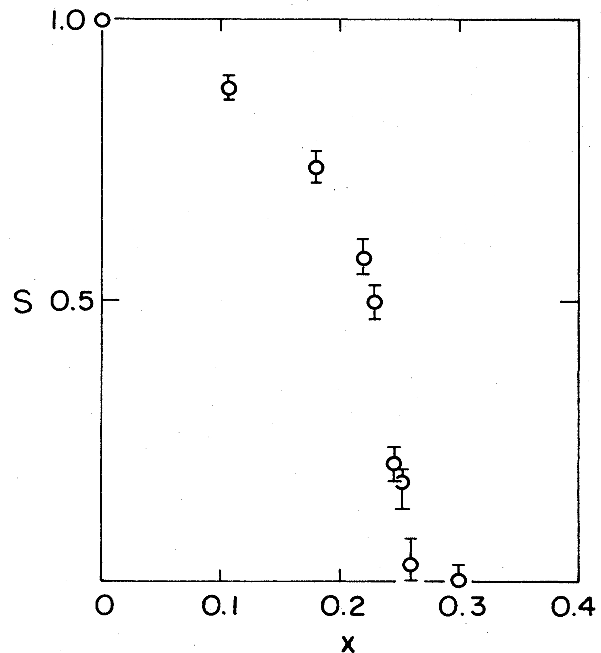

FIG. 3. The steady-state order parameter S as a function of x, as determined by planar growth in the [100] direction.

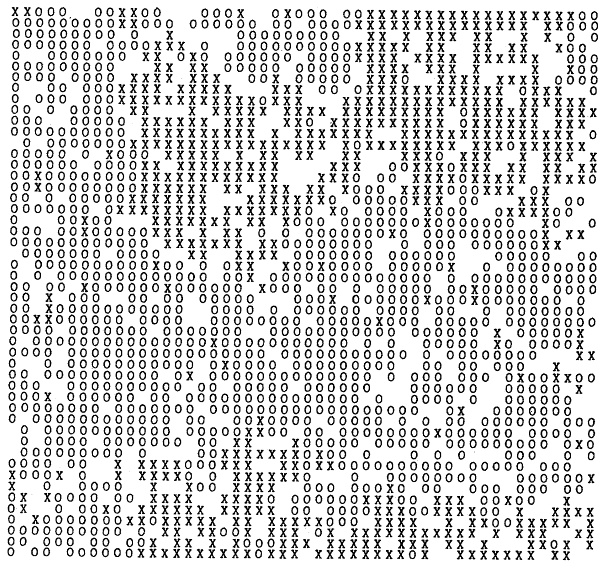

FIG. 4. The cross section of a crystal grown in the [100] direction from a disordered initial plane. Only one quarter (50×50) of the total plane (100×100) is shown. *O* and *X* represent Ga and As atoms, respectively, while Ge atoms are represented by blank spaces.

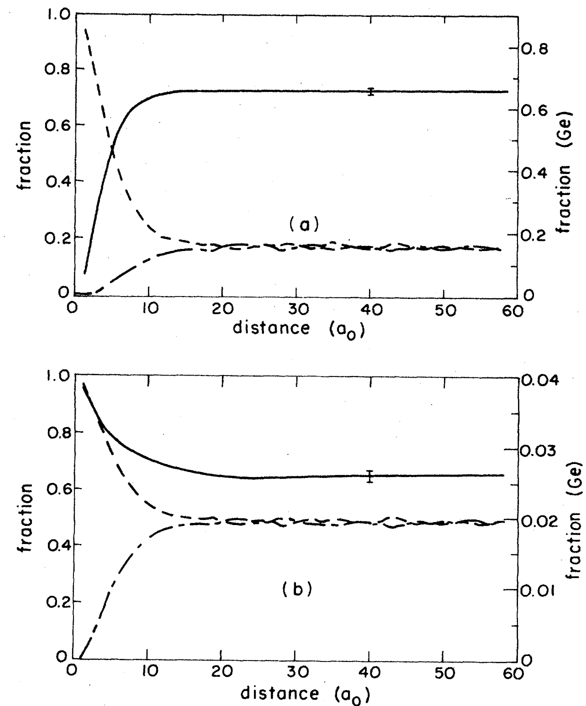

FIG. 5. The fractions of "right" (dashed line) and "wrong" (dashed-dotted line) atoms in a crystal grown in the [111] direction from an ordered initial plane, as functions of the distance from the initial plane. Also plotted by the solid line is the fraction of Ge atoms (a) in odd-numbered planes and (b) in even-numbered planes. $t=0.02$ and $x=0.34$. Fluctuations have been smoothed out, and the fluctuation is shown by error bars except when two curves are overlapping.

we find domains. Within each domain, the order parameter appears as big as that from the ordered initial state. One example is shown in Fig. 4. As there is no predefined right or wrong atom, different regions in the plane will have different atoms as the right atom. As a result, the fraction of one kind of atom, when averaged over the whole plane, is not as big as when averaged over the domain.

Some crystals were grown without applying the periodic boundary condition. The reasoning is as follows. The domains grow in size as the thickness increases; when there are only a few domains, they compete with one another. If the periodic boundary condition is loosened, the competition lessens at the boundary. As a result, the overall order parameter increases faster (than when the periodic boundary condition is applied), but a single domain is still not attained in several hundred layers of growth.

B. Planar growth in the [111] direction

There is one basic difference between growing the crystals in the [100] and growing them in the [111] direction: two different relations exist between neighboring planes in the [111] direction but only one in the [100] direction. As a result, neighboring planes in the [111] direction can have quite dissimilar structures. Figure 5 shows the fractions of Ga and As in odd- and even-numbered planes, with the initial plane considered to be plane 0. All the sites in the initial plane are filled with Ga and the parameter t is 0.02. In the steady state the odd-numbered planes have a small fraction of their sites filled with Ge (~ 0.02 at $t=0.02$), and the rest of the sites are divided equally between Ga and As. The even-numbered planes, on the other hand, have a quite large fraction of Ge (~ 0.66 at $t=0.02$). Although it is not easy to understand intuitively how the steady state is reached, it is possible to see how it is maintained. The sites in an even-numbered plane are determined by three already occupied nearest-neighbor sites and the probability of having both Ga and As is quite strong. When both Ga and As are nearest neighbors, the site is forced to have Ge and the plane gets a big fraction of Ge. A site in an odd-numbered plane, however, is restricted by only one nearest neighbor; moreover, most of the sites have Ge, which does not impose any restriction. As a result, the composition of an odd-numbered plane is largely determined by its unrestricted probabilities.

When the direction of growth is reversed, the results are the same, with odd and even reversed. Growth with different initial planes produces the same steady state. Varying the parameter t does not change the results qualitatively. It does change the final composition and the speed at which the steady state is reached. But no t value produces a steady state with a long-range zinc-blende order between the Ga and As atoms. There also is the problem of not being able to get a low Ge composition. Any finite t value produces a steady state with a big fraction of Ge. (If the initial plane is ordered, $t=0$ produces a perfectly ordered GaAs.) This model, therefore, predicts that epitaxial growth of the system in the [111] direction at low

Ge vapor pressure is not the dominant one. To develop the large Ge composition in the alternating planes would require a long time, and such a growth would occur very slowly. Other growth morphologies would more probably dominate, such as growth about nucleation sites, and one would expect a polycrystalline final state.

C. Spherical growth

Due to computational limitations, the crystals were grown only to a sphere of radius $20a_0$ which contained 268 057 sites. Because of this small radius, the steady state was not attained for the lower concentration values. As one "layer" does not have many sites and the statistical fluctuation is large, the numbers of right and wrong atoms in several layers were summed to reduce the statistical fluctuations. The results are shown in Fig. 6 for three different t values as a function of radius.

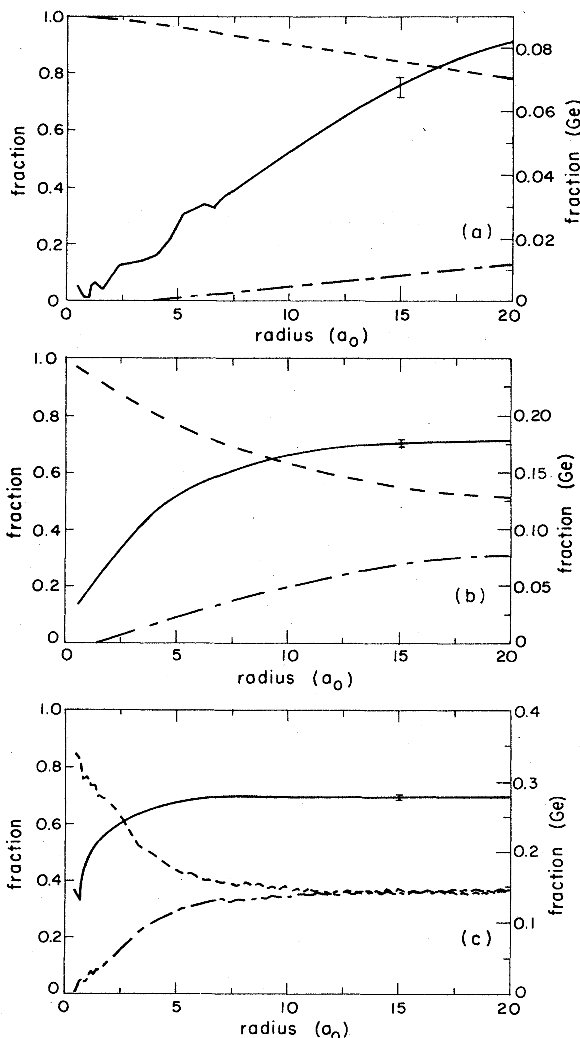

FIG. 6. The fractions of "right" (dashed line) and "wrong" (dashed-dotted line) atoms in a spherically grown crystal, as functions of the radius, in units of a_0. Also plotted by the solid line is the fraction of Ge atoms: (a) $t=0.005$, $x \geq 0.08$; (b) $t=0.03$, $x=0.18$; and (c) $t=0.08$, $x=0.28$. Fluctuations have been smoothed out, and the fluctuation is shown by error bars except when two curves are overlapping.

The Ge concentration reaches its steady-state value before the order parameter does. Thus at $x=0.18$ the Ge concentration has saturated at 18%, but the order parameter is still decreasing at the largest calculated radius of $20a_0$. Only when $x>0.28$ does the order parameter decay rapidly enough to reach its steady state, which is zero (Fig. 6). For $x<0.18$, even the Ge concentration has not attained saturation at the radius of $20a_0$.

In spite of this lack of saturation in the computer simulation, we can still make arguments about x_c. As the computer simulation for the [100] growth showed, and as shown below in the algebraic approximation, the decay length becomes shorter on either side of x_c. In the spherical growth case, the decay length is monotonically increasing as t and thus x decreases down to the smallest value of $t=0.005$ employed corresponding to $x=0.08$ at a radius of $20a_0$. For $x<0.18$ the Ge concentration has not saturated at $20a_0$, and so we do not know its value. However, we do know that we are above x_c since we find the decay length still increasing. Thus we can conclude that $x_c<0.18$ for the spherical growth case.

By making a heroic effort it would be possible to increase the maximum radius reached in the simulation, but since the number of sites increases as the cube of the radius, the gain would be very slow. We have already served our purpose by showing that x_c in the spherical growth is significantly smaller than in the (100) planar case. For these reasons we did not pursue the computer simulation further for the spherical growth case.

Growth with different initial conditions was not tried. Using As as the center atom is completely equivalent to using Ga. Using Ge as the center atom may produce interesting results, such as the formation of different domains of the ordered state, but the program is set up to study the correlation with the center atom only. When the center atom is Ge, the correlation around the center atom is symmetrical between Ga and As as no net order is present. Even if there are domains with orders within each domain, there will be no average long-range order. The study of each domain would be quite similar to the growth around Ga (or As) as the center atom.

IV. ANALYTICAL MODEL

It is possible to express the planar growth in recursion relations analytically if correlation within the planes is ignored. Even though the analytic form does not give exactly the same results as the computer simulation, it does show similar qualitative behavior. It shows, in the case of growth in the [100] direction, the existence of a critical composition x_c above which the long-range order disappears. The order parameter as a function of the composition x as determined by the analytic method has about the same shape as that obtained by the computer simulation. The analytic form for the growth in the [111] direction confirms the results obtained by the computer simulation in that direction, namely, that low x values cannot be reached with any finite t values.

It is rather difficult to study the behavior of the system by computer simulation when the parameter is close to the critical value, because the approach to the steady state is

slow. But the analytic method can be studied easily even when t is close to t_c.

A. Analytical study of growth in the [100] direction

Recursion relations for p and q, the fractions of Ga and As in a plane, can be derived in the following manner. The parameter t has the same meaning as in the computer simulation and correlation within each plane is neglected, but correlation between planes is included by the nearest-neighbor condition. Neglecting correlation within the plane greatly simplifies the problem. To test this statement, the correlation within a (100) plane was calculated from the computer simulation in the steady-state region. The values of the algebraic approximation with no correlation are compared in Table I with the actual numbers of pairs. There are more Ga-Ga and As-As and fewer Ga-As second-nearest neighbors than were calculated by the algebraic approximation. The number of pairs with one or two Ge atoms is about the same as in the algebraic approximation. Thus, there exists a correlation within the plane which is neglected in the algebraic approximation, but the error does not appear to be large. Note that this correlation reflects a weaker second-neighbor zinc-blende order which is 100% in the first neighbors.

Each site in a given plane is determined by two already occupied sites in the plane below and the probabilities of having both Ga and As, Ga(As) and possibly Ge, and only Ge are $2pq$, $p^2+2pr\,(q^2+2qr)$, and r^2, respectively, where $r=1-p-q$, the fraction of Ge.

Then the probabilities in the next plane, p' and q', are given by the following equations:

$$p'=\frac{1-t}{1+t}(q^2+2qr)+\frac{1-t}{2}r^2\ ,$$
$$q'=\frac{1-t}{1+t}(p^2+2pr)+\frac{1-t}{2}r^2\ . \tag{1}$$

Now, we will define new variables $u=p+q$ and $v=p-q$. If a steady state is reached, $1-u$ is equal to x, the fraction of Ge, and v is the order parameter. The recursion relations for u and v are given as

$$u'=\frac{1-t}{1+t}(2u-\tfrac{3}{2}u^2+\tfrac{1}{2}v^2)+(1-t)(1-u)^2\ ,$$
$$v'=-\frac{1-t}{1+t}v(2-u)\ . \tag{2}$$

When a steady state is reached, we will expect to have $u'=u=u_f$ and $v'=-v=v_f$. The equations for the steady-state values are

$$u_f=\frac{1-t}{1+t}(2u_f-\tfrac{3}{2}u_f^2+\tfrac{1}{2}v_f^2)+(1-t)(1-u_f)^2\ ,$$
$$v_f=\frac{1-t}{1+t}v_f(2-u_f)\ . \tag{3}$$

It is apparent from the second equation of (3) that $v_f=0$ is one solution. If we assume $v_f\neq 0$, we get the following equation by substituting the second part of (3) into the first:

$$v_f^2=-x^2-2x+1-\left[\frac{2x^3}{2+x}\right] \tag{4}$$

with $x=1-u_f$.

Equation (4) has a solution only when the right-hand side is positive. The zero of the right-hand side is $x=0.395\,794\ldots$. The t corresponding to this x is $0.165\,203\,3\ldots$. When x is smaller than x_c, the right-hand side of (4) is positive and it has a solution. For $x<x_c$, the order parameter v_f can be determined (Fig. 7) as a function of x, the Ge fraction. When $x>x_c$, $v_f=0$ is the only solution, and the relation between t and x in this region is given by the following equation:

TABLE I. The probability of occurrence of a given pair of atoms as neighbors in the (100) plane, for two x values. The numbers in the simulation columns are determined by counting actual occurrences in the computer simulation, and those in the algebraic columns are the values calculated by the algebraic approximation used in the text. (*Note*: Two significant digits are shown and, due to roundoff errors, the numbers do not necessarily add up to 1.)

	$x=0.38$, $p=0.31$, $q=0.31$		$x=0.18$, $p=0.78$, $q=0.04$	
	Simulation	Algebraic	Simulation	Algebraic
Ga-Ga	0.14	0.096	0.63	0.61
As-As	0.14	0.096	0.011	0.0016
Ge-Ge	0.15	0.14	0.037	0.032
Ga-As	0.12	0.19	0.039	0.062
Ga-Ge	0.23	0.24	0.26	0.28
As-Ge	0.22	0.24	0.020	0.014

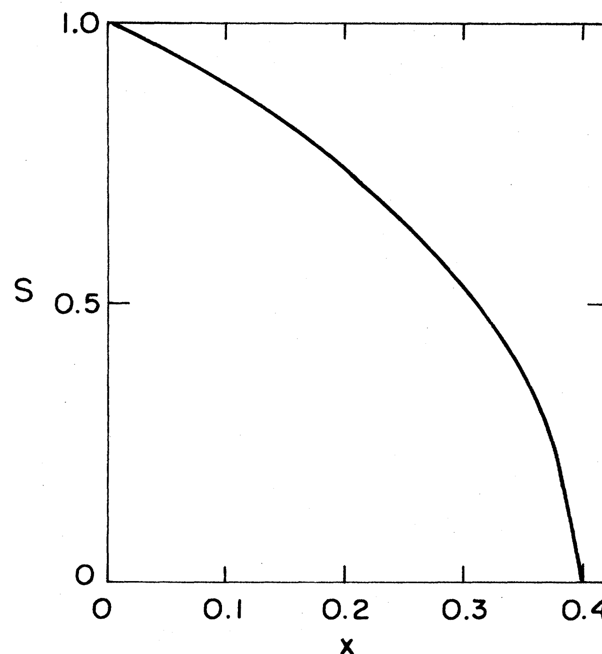

FIG. 7. The order parameter as a function of x, as determined by the algebraic approximation for growth in the [100] direction.

$$(1-t)(1-2t)x^2-4x+(1+3t)=0 . \quad (5)$$

When $x<x_c$, $v_f=0$ is also a solution, in addition to the solution of (4). It is, however, an unstable one. If v is slightly different from zero initially, v_f is again given by (4). This is what happens in the computer simulation. In the computer simulation, and in an actual growth, the order parameter will not be exactly equal to zero, due to statistical fluctuations. As a result, if $x<x_c$, the steady state will be ordered even if the initial plane is disordered.

Now we examine the behaviors of the order parameter when x is close to x_c. When $x \lesssim x_c$, we will start from (4). The right-hand side of (4) is analytic at $x=x_c$ and can be expanded in a series. As it is zero at $x=x_c$ and its derivative is nonzero and negative, we can write it in the following way:

$$v_f^2=-c^2(x-x_c)+\text{higher-order terms} . \quad (6)$$

From this we get the following relation, when $x \lesssim x_c$:

$$v_f \simeq c(x_c-x)^{1/2} . \quad (7)$$

When $x \gtrsim x_c$, the approach to the steady state, which is without a long-range order, is expected to be slow. At $x=x_c+0.01$, it takes about 57 and 109 planes for the order parameter to change from 1 to 0.1 and 0.1 to 0.01, respectively. (Four planes are equivalent to the growth of one conventional cubic lattice constant.) At $x=x_c+0.04$, it takes only 19 and 27 planes for the same results. When the order parameter is small and x is close to x_c, we can write the order parameter in the following form:

$$S(n)=S(0)\exp(-n/\xi) . \quad (8)$$

If we calculated from the number of planes needed for the order parameter to change from 0.1 to 0.01, we get $\xi=47.4$ and 11.7 for $x=x_c+0.01$ and $x_c+0.04$, respectively.

We can also get an expression for the order parameter directly from the recursion relation. From the second equation of (2), we get

$$S(n)=aS(n-1)=a^nS(0) \quad (9)$$

with

$$a=\frac{1-t}{1+t}(1+x) .$$

Comparing (8) and (9), we get

$$\xi=\frac{-1}{\ln a} . \quad (10)$$

The values of ξ obtained in this manner for $x=x_c+0.01$ and $x_c+0.04$ are 48.1 and 11.7, respectively. They are in good agreement with the ones obtained from the numerical iteration.

Lastly, we can get the critical index for the order parameter in the vicinity of the critical point. In the vicinity of x_c, a can be expanded in the following form:

$$a=a(x_c)+(x-x_c)\frac{da}{dx}(x_c)+\text{higher-order terms} , \quad (11)$$

with $a(x_c)=1$ and $(da/dx)(x_c)\simeq -2.06$.

Substituting (11) into (10), we get

$$\xi(x) \simeq 0.485(x-x_c)^{-1} .$$

Therefore, the correlation length ξ is given by a simple pole singularity at the critical point; i.e., the critical exponent is 1. The critical behavior of the (100) growth is summarized in Table II. The results of the algebraic approximation are mean free values since no fluctuations are present.

TABLE II. Summary of critical behavior for the [100] growth case. $S(x)$ is the long-range zinc-blende order parameter as a function of concentration x. $S(n)$ is the long-range zinc-blende order as a function of the number of (100) planes from the initial ordered plane.

$x<x_c$:	$S(x)\sim(x_c-x)^\beta$: $\beta=\frac{1}{2}$
$x>x_c$:	$S(n)=S(0)\exp(-n/\xi)$
	$\xi(x)\sim(x-x_c)^{-\nu}$: $\nu=1$

B. Analytical study of growth in the [111] direction

We will assume that the direction of growth is such that the sites in the first plane are exactly on top of the sites in the zeroth plane. If the direction of the growth is reversed, it is equivalent to having f_0 and g_0 as the initial condition, as defined below, instead of p_0 and q_0. The steady state is the same regardless of the direction of the growth.

We will call the fractions of Ga and As in the even-numbered planes p and q. Those in the odd-numbered planes will be called f and g. The recursion relations can be derived in a way similar to the case of the [100] direction. The results are given below, with $r=1-p-q$ and $h=1-f-g$:

$$\begin{aligned} f&=\frac{1-t}{1+t}q+\frac{1-t}{2}r ,\\ g&=\frac{1-t}{1+t}p+\frac{1-t}{2}r ,\\ p'&=\frac{1-t}{1+t}(f^3+3f^2h+3gh^2)+\frac{1-t}{2}h^3 ,\\ q'&=\frac{1-t}{1+t}(f^3+3f^2h+3fh^2)+\frac{1-t}{2}h^3 . \end{aligned} \quad (12)$$

It was not possible for us to find the steady state algebraically. But numerical iterations indicated that the only steady state for all values of nonzero t is the one with $f=g$ and $p=q$, but $f\neq p$. This steady state is one with no long-range zinc-blende order between the Ga and As atoms, and the structure of even-numbered planes and odd-numbered planes is different. For $t\neq 0$, the minimum value x we can obtain is 0.375. As t increases from 0^+ to 1, a_f decreases from 0.5 to 0, and p_f increases from 0.125 to about 0.158 and then decreases to 0. The fact that $x<0.375$ is not attainable is in qualitative agreement with the results of the computer simulation.

V. DISCUSSION AND CONCLUSIONS

We have shown through our model that the nonuniqueness of x_c for a metastable alloy of the form $(GaAs)_{1-x}(Ge_2)_x$ can be explained in terms of varying morphologies of kinetic growth. Although the critical composition x_c in a spherical growth was not determined precisely, an upper bound is set. The value is smaller than that of a planar growth in the [100] direction.

We investigated the behavior of the long-range order parameter S as a function of x for a planar growth in the [100] direction. The critical composition x_c obtained in this way is in reasonable agreement with the experimental results.

Explanations of the transition from zinc-blende to diamond structure have been presented previously.[2,3,15] However, they do not account for the nonuniqueness of the critical composition x_c. References 2 and 3 based their discussions on a thermodynamic transition. For the metastable alloys discussed here a kinetic model[8] as expanded here is more appropriate. Reference 15 identified the zinc-blende to diamond transition with the percolation transition of infinite chains of Ga—As—Ga—As... bonds. This predicts a unique value of $x_c = 0.57$, in disagreement with the experimental results. Percolation theory does not account for different growth conditions.

The model employed in Ref. 4 also assumed perfect short-range order, but differs from the one employed here by not allowing variations due to growth morphology and by requiring the Ga and As atoms always to form Ga—As bonds. Thus, the possibility of a Ga or an As completely surrounded by Ge is not allowed for in this model. The model predicts similar percolation properties to those of Ref. 15 and, in particular, the zinc-blende to diamond transition was predicted around $x_c = 0.75$ without any dependence on the method of growth. Thus, this model shows the same inadequacies as that of Ref. 15.

It is useful to emphasize the distinction between our model and the percolation theories. In our model the sample grows layer by layer, and the restrictions imposed by the short-range-order conditions depend on the orientation of the layers. In the percolation theories, the sample is built up throughout its volume and no possible variation with growth morphology is allowed for.

We point out that the planar growth in the [100] direction has the character of a cellular automata problem. The algorithm of growth $x < x_c$ produces an ordered state regardless of the initial state. The introduction of a probability in the problem is not new, and has been used before.[12]

Finally, algebraic approximations were used to show the features of the planar growth cases. They show the general behavior of the computer simulations. The numerical agreement is only approximate, which is expected because of the neglect of the correlation among sites within the plane. The counting of the actual number of pairs shows that there is a correlation among them. The critical behavior is calculated and the values of critical indices are the mean-field values. This is not surprising, because our algebraic equation makes no allowance for fluctuation.

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