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Structure and phase transitions of grown and equilibrated alloys

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We explore the relationship between cellular-automata-based growth models and equilibrium thermodynamic models of material structure. Application is to the growth of $(\mathrm{GaAs})_{1-x}\mathrm{Si}_{2x}$-type alloys. As a function of x these alloys have an order-disorder phase transition. We address a controversy over the relevance of growth models or equilibrium statistical models to the description of the alloy structure, and particularly the critical properties of the phase transition. Experiments to determine the relevance of the models are proposed.

In 1982 a new class of mixed alloys with interesting structural and electronic properties was grown by sputtering techniques.[1] These alloys consist of a mixture of III-V compounds and group-IV elements such as $(\mathrm{GaAs})_{1-x}\mathrm{Si}_{2x}$. The materials would phase separate under true equilibrium conditions but under the conditions of growth they form a mixed alloy with the atoms forming a diamond lattice. As a function of x such materials may be expected to undergo a type of structural phase transition.[2] In the $x \rightarrow 0$ limit the Ga and As sublattices are well defined, while in the $x \rightarrow 1$ limit there are no sublattices defined. Indeed, at $x \approx 0.3$ experimentally[3] a change in the long-range-order parameter has been observed by x-ray diffraction for materials grown in the [100] direction.[2] Two distinct types of theories have been proposed for the structure of these alloys and particularly for this transition.

In the first type of model,[2,4] a (metastable) thermodynamic equilibrium is postulated (with phase separation excluded). A model Hamiltonian describes the local interactions of atoms on adjacent sites, where qualitatively As—As bonds and Ga—Ga bonds are high in energy, Ga—As bonds are low in energy, Ga—Si and As—Si bonds are intermediate. The effective Hamiltonian is equivalent to a three-state model on a diamond lattice, where the three states on each site are the three possible atoms on a site. The phase diagram of this Hamiltonian including an order-disorder phase transition is analyzed with fitted interaction parameters to describe a phase transition in the GaAs to Si alloy system. This model then yields structural information such as local bonding probabilities that can be used to study other properties of the system such as the electronic states.

In the second type of model[3,5] a simple probabilistic growth model[6] is used. In this model the atoms are added layer by layer using assumed sticking probabilities for the three different atoms at the growth face. The sticking of As atoms to As atoms or Ga atoms to Ga atoms is forbidden, and Si sticks with uniform probability. These rules are equivalent to a three-state probabilistic cellular automaton (CA) describing a new layer in terms of the preceding layer atoms. Each layer of the grown material represents a "snapshot" of the CA. A grown sample corresponds to a particular time history of the CA. No equilibration is allowed after deposition. The growth model yields a bulk material whose structural properties include a phase transition in the long-time limit of the automaton as a function of Si concentration. In the ordered phase, the long-time limit of the growth model is a two-cycle, alternating between layers dominated by arsenic and gallium, respectively. Similar to the thermodynamic model, the long-range-order parameter measures this sublattice correlation.

Nominally these two models correspond to different dynamics (Fig. 1). The equilibrium model describes a

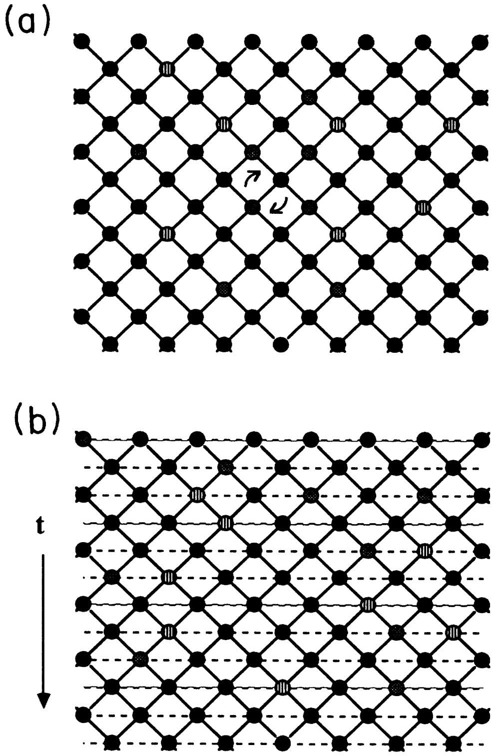

FIG. 1. Schematic illustration of the difference between two classes of models of material structure (a) equilibrium and (b) simple growth automata rule. In equilibrated material the atoms are considered able to move around, as illustrated by atomic interchange but typically effected also by defect motion or other dynamical processes. In material modeled by simple growth rules, the layers are added strictly according to a layer-by-layer process. The configuration of each layer depends only on those preceding it. The illustrated alloy has three components.

material where atomic motion allows the exploration of phase space by atoms for a duration long enough to attain equilibrium statistics. Practically, it is possible that equilibration occurs only during and close to the time of deposition, in which case the net deposition time of a layer must exceed the relaxation time to equilibrium. The growth-model dynamics are for precise sticking probabilities at the growth face; it is assumed that after sticking no reorganization of atoms occurs. The microscopic dynamics of the actual growth process are not established.

While the controversy over which model to accept has continued for several years, much of the focus has been on the electronic properties[7–11] that are derived from the structural properties by only approximate electronic Hamiltonians, whose solution is a controversy in itself.

In this article we analyze more directly the structural implications of these two models and propose experimental tests to better understand the relevance of simple growth models based on Cellular Automata and thermodynamic equilibrium models to the structure of materials. We first discuss the formal relationship between CA growth models and Hamiltonians. Specializing to the case of $(\mathrm{GaAs})_{1-x}\mathrm{Si}_{2x}$ alloys, a formal relationship between the two models is explicitly constructed. This leads to a discussion of generic features of these models, with experimental implications that can distinguish their relevance.

AUTOMATA AND HAMILTONIANS

For a material in equilibrium, the Hamiltonian specifies the probability of any microstate of the system through the Boltzmann weight. When equilibration time is much faster than the measurement time, then, in the course of a measurement, the system is able to move through phase space in a manner that the time spent in each region is proportional to the corresponding Boltzmann weight. If the system is in a quenched (frozen) equilibrium distribution, or the equilibration time is slower than measurement time, then the Boltzmann weight can still be realized when a material is composed of many independent subsystems (for example, crystal grains or correlation lengths) or when averaging explicitly over many measurements of independent samples.

In contrast, a CA-based growth model assumes a very different scenario. Deposition of a single layer occurs according to local stochastic rules. These rules specify the probability of attaching each kind of atom to every possible atomic environment specified by the previous layer. Once the layer has been added, no further equilibration is allowed to occur; that is, the time scale of equilibration is much longer than that of the growth, or any experiment. Nevertheless, it is easy to show that the local stochastic growth rules can be reinterpreted as the Boltzmann weight of a properly defined Hamiltonian.[12,13] Thus, when a material is composed of many independent subsystems or when averaging explicitly over many measurements this inferred Boltzmann weight is realized.

Consider a probabilistic CA rule and its time history [Fig. 1b]. The CA rule is defined by a probabilistic rule of discrete time $P(\mathbf{s}(\mathbf{x}^d, t+1)|\mathbf{s}(\mathbf{x}^d,t))$. $\mathbf{s}(\mathbf{x}^d,t)$ completely specifies the d-dimensional system at time t. Then the probability of having a state $\mathbf{s}(\mathbf{x}^d, t+1)$ of the system at a later time $t+1$ is given by

$$P(\mathbf{s}(\mathbf{x}^d, t+1))=P(\mathbf{s}(\mathbf{x}^d, t+1)|\mathbf{s}(\mathbf{x}^d,t)) \ .$$

Each time slice of the automaton is stored or "frozen" as a layer of a material grown layer by layer; the time axis of the CA plays the role of the spatial growth direction. The d-dimensional automaton is related to a $(d+1)$-dimensional system Hamiltonian by its interlayer interactions,[13] given by

$$-\beta H_{\mathrm{CA}}[(s(\mathbf{x}^{d+1}))]=\sum_t \ln[P(\mathbf{s}(\mathbf{x}^d, t+1)|\mathbf{s}(\mathbf{x}^d,t))] \ .$$

An ensemble of materials, grown using the probabilistic cellular automaton, is identical by construction to the equilibrium distribution of the Hamiltonian H_{CA}. This construction leads to a mapping of all d-dimensional cellular automata to $(d+1)$-dimensional Hamiltonians,

$$\mathrm{CA}^d \to H^{d+1} \ .$$

If this mapping is interpreted simplistically, there would seem to be *no* difference between the two types of models: material grown by the cellular-automaton rule can also be described as the result of equilibration of a Hamiltonian.

COMPARISON OF HAMILTONIANS FOR TWO MODELS

The CA rule proposed[5] by Kim and Stern (KS) for describing growth of $(\mathrm{GaAs})_{1-x}\mathrm{Si}_{2x}$ is defined on a diamond lattice by excluding Ga-Ga sticking and As-As sticking and assuming all other sticking is unity but controlled by the relative Si vapor fraction p. To write this formally, specify the type of atom added using a three-state variable s for the time slice $t+1$, and σ_i are the three-state variables of its neighbors already present at the previous time t. s or $\sigma_i=0$ corresponds to silicon, ± 1 corresponds to Ga and As, respectively. The spatial relationship between these variables is shown in Figs. 2 and 3.[15] With these definitions, the probabilities of adding each of the atom types in terms of the previous layer may be expanded as

$$\ln P(s|\sigma_1\sigma_2)=as^2+b(\sigma_1^2+\sigma_2^2-\sigma_1\sigma_2)+\frac{c}{2}\sigma_1\sigma_2(1-\sigma_1\sigma_2) -d[s\sigma_1(1+s\sigma_1)+s\sigma_2(1+s\sigma_2)]+f \ , \tag{1}$$

$$e^f=p \ ,$$

$$e^a=\frac{1-p}{2p} \ ,$$

$$e^b=\frac{2}{1+p} \ ,$$

$$e^c=\frac{8p}{1+p^3} \ ,$$

$$d=\infty \ .$$

The second-neighbor terms involving $\sigma_1\sigma_2$ are generated

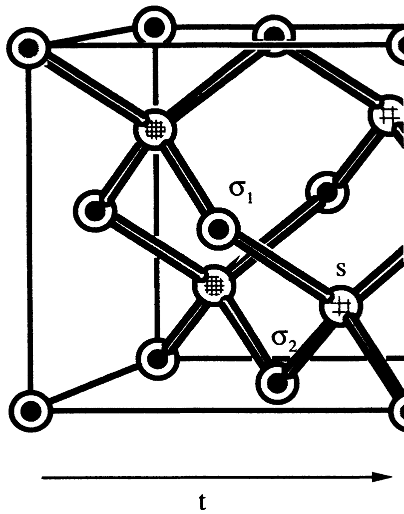

FIG. 2. Illustration of the diamond lattice. For a (100)-growth automaton the layers are grown from dark to light shading (left to right). In the ordered GaAs (zinc-blende) -like phase the shaded sites are one sublattice and the crosshatched sites are the other sublattice. The relationship between a site s and its predecessor neighbors σ_1,σ_2 is shown. The growth model (Ref. 5) for $(\mathrm{GaAs})_{1-x}\mathrm{Si}_{2x}$ introduces effective interactions between σ_1,σ_2 which break the symmetry of the lattice and are relevant at the critical point changing the critical behavior.

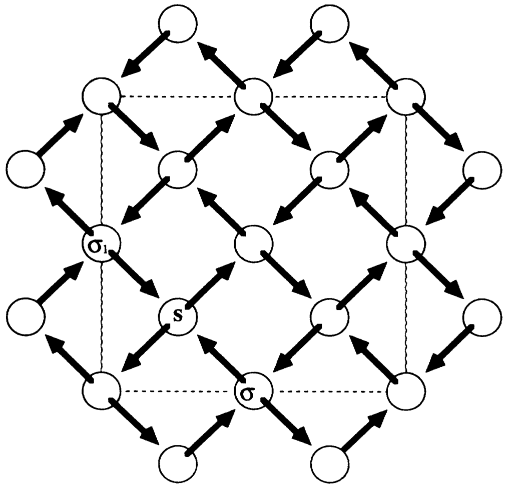

FIG. 3. Illustration of the influence of sites where the growth direction is perpendicular to the plane of the drawing (Ref. 15). Arrows indicate the directional bonds from one atom to the two atoms that it influenced in the growth process. The dashed line is the projection of the cubic cell of the diamond lattice.

by the interference of restrictions placed on the addition of an atom by the two σ sites.[16]

The three-dimensional Hamiltonian that corresponds to this growth model is

$$-\beta H_{\mathrm{CA}}=(a+2b)\sum s_i^2-d\sum_{\mathrm{NN}} s_is_j(1+s_is_j)+\left[\frac{c}{2}-b\right]\sum_{\mathrm{NNN}}{}' s_is_j-\frac{c}{2}\sum_{\mathrm{NNN}}{}' s_i^2s_j^2+\beta F\ , \tag{2}$$

with $\beta=(k_BT)^{-1}$ and $F=Nf=N\ln p$, where N is the total number of sites. The second-neighbor interactions (or next nearest neighbors, NNN) are only summed over a restricted class of second neighbors. First, they must lie in a plane parallel to the growth plane. Second, they must be related to a mutual nearest neighbor that succeeds them in the growth direction (see Figs. 2 and 3).

The Newman-Dow (ND) equilibrium-model[4] Hamiltonian is written as

$$H_{\mathrm{eq}}=h\sum s_i+\Delta\sum s_i^2+J\sum_{\mathrm{NN}} s_is_j+K\sum_{\mathrm{NN}} s_i^2s_j^2\ .$$

There are three basic differences between these two Hamiltonians. Of these, two do not reflect fundamental differences between equilibrium and CA-based models.

The first difference is the divergent nearest-neighbor interaction in the KS model compared to its finite value in the ND model. This directly corresponds to an exclusion of nearest-neighbor As-As and Ga-Ga pairs in the former and their inclusion in the latter. The difference in local environment (nearest neighbor) has attracted much attention in the electronic-structure calculations in an attempt to distinguish the validity of the two models. However, this is not a fundamental difference between growth and equilibrium models.[17] Such comparisons do not distinguish the inherent validity of a growth versus equilibrium model for the structure of the material, only the particular choice of interaction parameters, or sticking probabilities.

The second difference is the importance of second-neighbor interactions in the KS growth model. Such second-neighbor interactions could be included in the ND model, and generally should exist in Hamiltonian systems. Nevertheless, any comparison of these models on the basis of an extended parameter space should recognize their relative simplicity of specification. In the KS model only one parameter describes the whole Hamiltonian consisting of three finite interactions. Later growth models for more realistic results, however, have chosen to complicate the parameter space.[18]

The third major difference is the asymmetry of the interactions. Specifically, the asymmetry of the second-neighbor interactions in the growth-model Hamiltonian. This asymmetry, unlike the first two differences, is a fundamental difference between a growth approach and generic thermodynamic approach. It suggests that specific tests for the applicability of growth versus thermodynamic models be based on the asymmetry of the material structure or related properties.[6,19]

CRITICAL PROPERTIES AND EXPERIMENTAL TESTS

A concrete example of the asymmetric properties of the automata growth model in contrast to the thermodynamic model is provided by the critical properties of the order-disorder transition.

The properties of Hamiltonians derived from CA rules are unusual in several ways.[12,16,20–23] A key property of this class of Hamiltonians is that the free energy of the Hamiltonian is analytic.[16] Indeed, as defined, it is identically zero.[22] This can be seen by taking a free-energy trace with the formal definition of the Hamiltonian and using the normalization $\sum P = 1$. It is usual, however, to expand the expression for the Hamiltonian in interaction terms [Eq. (2)], leaving the constant term as the free energy. This yields a nonzero free energy that is *analytic* as a function of Hamiltonian or CA parameters. While phase transitions are normally associated with nonanalytic free energies, anomalous transitions may occur with analytic free energies.[12,21,22] The phase transition described by KS as a function of p in Eq. (2) is such a phase transition.

The critical exponents of the automata growth model can be found from quite general arguments discussed by Grinstein *et al.*[23] In order to apply their discussion, the growth-model phase transition must be equivalent to a ferromagnetic transition in the steady-state limit of an automaton with up-down symmetry. This equivalence can be shown in two ways. By considering every other layer (tracing over the intermediate ones) the long-time limit of the growth model becomes a steady state rather than a two-cycle, and the order parameter is ferromagnetic in each layer (s_i). Alternatively, the limit two cycle can be converted to a one-cycle (steady state) by redefining the spin variables on alternate layers sending $+1 \leftrightarrow -1$. Having established the equivalence, the discussion of Grinstein *et al.*[23] implies that the universality class of the phase transition is equivalent to that of the dynamical Ising model. The mean-field results for the critical exponents of this transition are $\nu = 0.5$ perpendicular to the growth direction and $\nu_\tau = z\nu = 1$ in the growth direction; whereas the exact value perpendicular to the growth direction[24] is $\nu = 1$ and the best value in the growth direction[25,26] is $\nu_\tau = z\nu = 2.10 \pm 0.05$. In the simulations of Kim and Stern[5] the exponent ν_τ is found to agree with the mean-field value $\nu_\tau = 1$. This suggests that the stability of the Ising fixed point discussed by Grinstein *et al.*[23] does not extrapolate from $d = 4 - \epsilon$ down to the physical dimension of $d = 2$.[27] This however, does not explain why the exponents found by Kim and Stern are mean-field-like. In any case, the ratio $\nu_\tau / \nu = z \approx 2$ is large. This is a significant difference that should be observable both experimentally and in simulations. Note that if an equilibrium model holds, $\nu_\tau / \nu = 1$ should be found.

The experimental detection of the difference in critical exponents requires the measurement of a set of samples grown with different compositions near the critical point. The asymmetry itself may be measurable on a single sample as a difference in the correlation length measured parallel and perpendicular to the substrate. Because of dislocations or grain boundaries, which are outside the consideration of these models, and also lead to anisotropy, this is not a fully conclusive test of the relevance of the two models. Measurement of the critical exponents would give a conclusive comparison. This requires a comparison of the static structure factor $\chi(\mathbf{q})$ for a series of samples in the vicinity of the phase transitions where the divergence of the correlation length can be measured and compared in different directions.

The experimental measurements may actually tell us more since the dynamics of growth may reflect an intermediate course between the two models. In reviewing the growth conditions,[1] it appears safe to suggest that the growth dynamics are not a direct sticking, nor do they support an equilibrium over long-length scales. The growth, occurring at a rate of 1 layer per second is likely to involve many growth-etching steps as has been discussed for the case of diamond thin films.[28] In such a multiple regrowth process, low-energy structures are preferentially retained. This suggests a quasiequilibrium approach for distances smaller than the growth-etching thickness fluctuations, consistent with the equilibrium[4] picture. At longer length scales, greater than the thickness fluctuations during multiple regrowth, the growth CA approach[5] would be relevant. Making use of the above arguments, the critical exponents of the order-disorder phase transition should display a crossover behavior near the critical point from thermodynamic spherically symmetric behavior to growth related asymmetric behavior when the correlation length extends beyond the equilibration size. Experimental tests can thus provide insight into the growth dynamics by focusing on the asymmetric properties of material structure at the phase transition.

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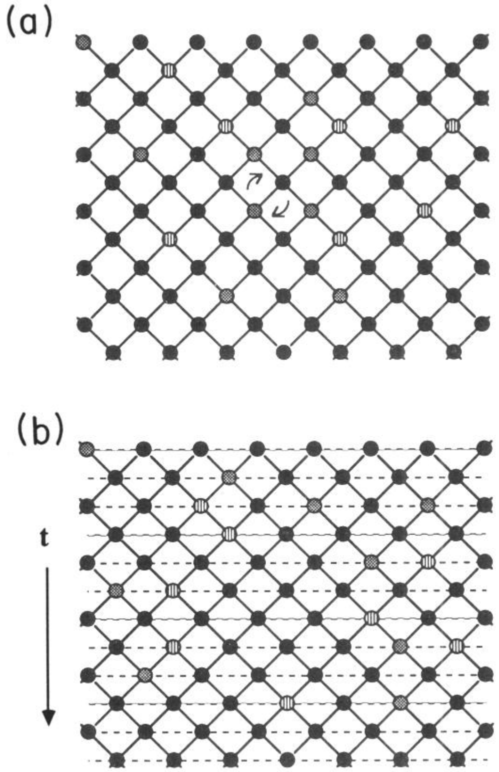

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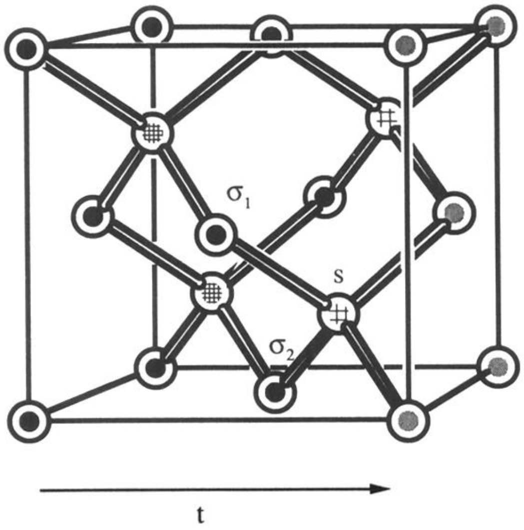

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