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Model for crystallization kinetics: Deviations from Kolmogorov–Johnson–Mehl–Avrami kinetics

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We propose a simple and versatile model to understand the deviations from the well-known Kolmogorov–Johnson–Mehl–Avrami kinetics theory found in metal recrystallization and amorphous semiconductor crystallization. We analyze the kinetics of the transformation and the grain-size distribution of the product material, finding a good overall agreement between our model and available experimental data. The information so obtained could help to relate the mentioned experimental deviations due to preexisting anisotropy along some regions, to a certain degree of crystallinity of the amorphous phases during deposition, or more generally, to impurities or roughness of the substrate. © 1999 American Institute of Physics. [S0003-6951(99)02641-8]

The interest in thin-film transistors made of polycrystalline silicon and silicon germanium has been driven by the technological development of active matrix-addressed flat-panel displays¹ and thin-film solar cells.² In this context, the capability to engineer the size and geometry of grains becomes crucial to design materials with the required properties. Crystallization of these materials takes place by nucleation and growth mechanisms: Nucleation starts with the appearance of small atom clusters (*embryos*). At a certain fixed temperature, embryos with sizes greater than a critical one become stable nuclei; otherwise, they shrink and eventually they vanish. Such a critical radius arises from the competition between surface tension and free-energy density difference between amorphous and crystalline phases (which favors the increasing of grain volume) yielding an energy barrier that has to be overcome to build up a critical nucleus. Surviving nuclei grow by incorporation of neighboring atoms, yielding a moving boundary with temperature-dependent velocity that gradually covers the untransformed phase. Growth ceases when growing grains impinge upon each other, forming a grain boundary. The final product consists of regions separated by grain boundaries. This simple picture has, however, two problems: On the one hand, this theory of nucleation and growth predicts an energy barrier far from the experimental value so nucleation would hardly be probable at available annealing temperatures.³ On the other hand, it is known that in crystallization of Si over SiO₂ substrates, nucleation develops in the Si/SiO₂ interface due to inhomogeneities or impurities that catalyze the

transformation.⁴ Therefore, a theory of homogeneous nucleation and growth is not entirely applicable to the referred experiments.

The transformation kinetics is also problematic. It is generally accepted that the fraction of transformed material during crystallization, $X(t)$, obeys the Kolmogorov–Johnson–Mehl–Avrami (KJMA) model,⁵ according to which $X(t) = 1 - \exp(-At^m)$, where A is a nucleation- and growth-rate-dependent constant and m is an exponent characteristic of the experimental conditions. Two well-defined limits have been extensively discussed in the literature: When all the nuclei are present and begin to grow at the beginning of the transformation, the KJMA exponent m is equal to 2 (in two dimensions), and the nucleation is termed *site saturation*. The product microstructure is tessellated by the so-called Voronoi polygons (or Wigner–Seitz cells). On the contrary, when new nuclei appear at every step of the transformation, $m = 3$ and the process is named *continuous nucleation*. Plots of $\log[-\log(1-X)]$ against $\log(t)$ should be straight lines of slope m , called KJMA plots. The validity of the KJMA theory has been questioned in the last few years,⁶ and subsequently several papers have been devoted to check it in different ways.^{7–9} However, those theoretical results still leave some open questions: For example, an exponent between 2 and 3 is experimentally obtained in two dimensions, the KJMA plots from experimental data do not fit a straight line in some cases,^{10,11} and the connection between geometrical properties (grain-size distributions) and the KJMA exponent is not clear.

In this letter, we show that these questions may be answered by assuming that nucleation is heterogeneous, not in a phenomenological way as in other proposed models,¹² but

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sticking to the basic ideas due to Cahn¹³ and Beck:¹⁴ The material is not perfectly homogeneous but contains regions with some extra energy (regions with some order produced during deposition, or substrate impurities) at which nucleation is more probable. Accordingly, we introduce a computational model consisting of several simple irreversible rules, with the additional advantage that it describes simultaneously space and time evolution. Furthermore, it allows us to average over a large number of realizations in very short computational times as compared to other computer models (see the recent review by Rollett¹⁵ for an overview of simulation models of recrystallization).

The model is defined on a two-dimensional lattice (square and triangular lattices were employed) with periodic boundary conditions. Every lattice site (or node) \mathbf{x} belongs to a certain grain or state, $q(\mathbf{x}, t) = 0, 1, 2, \dots$, the state 0 being that of an untransformed region. The lattice spacing is a typical length scale related to the available experimental resolution. Following the idea that the amorphous phase has random regions in which nucleation is favored, we choose a fraction c of the total lattice sites to be able to nucleate. We term these energetically favorable sites *potential* nuclei. These potential sites may be interpreted as random sites on a region where order is present, not just an isolated critical cluster. Initially, $q(\mathbf{x}, 0) = 0$ for all lattice sites \mathbf{x} and the system evolves by parallel updating according to the following rules: (i) A transformed site remains in the same state [$q(\mathbf{x}, t + \Delta t) = q(\mathbf{x}, t) \neq 0$]. (ii) An untransformed *potential* site may become a new nonexistent state (i.e., crystallizes) with probability n (nucleation probability), if and only if there are no transformed nearest neighbors around it. (iii) An untransformed site (including potential sites) transforms to an already existing transformed state with probability g (growth probability), if and only if there is at least one transformed site on its neighborhood. The new state is randomly chosen among the neighboring grain states.

For the model parameters, we expect a functional form $n \sim e^{-E_n/k_B T}$ and $g \sim e^{-E_g/k_B T}$, where E_n and E_g are the energy barriers of nucleation and growth, respectively. Hence, temperature is implicit in the definition of n and g . Figure 1 shows the microstructure at two different stages for two different sets of parameters. As we are interested in this letter in how different nucleation conditions yield different KJMA exponents and different microstructures for isothermal experiments, we define a characteristic time τ as the time that a grain needs to increase its size by one lattice site, and consequently, we can put $g = 1$. The simulation time step is, therefore, this characteristic time τ .

We have simulated 1000×1000 triangular and square lattices and averaged the outcome of 50 different realizations for each choice of parameters (characteristic simulation times are about 15–45 min in a Pentium II personal computer). The main results are the following: If $c \leq 1$, then most sites are potential sites, so new grains are able to nucleate at every stage of the transformation (continuous nucleation). On the contrary, when $c \ll 1$, and $n \leq 1$, every potential site nucleates at the early stages of the process (site saturation). Obviously, intermediate values yield a mixed behavior. Interestingly, the model parameters tune the KJMA exponent between 2 and 3. It is important to note that for small values

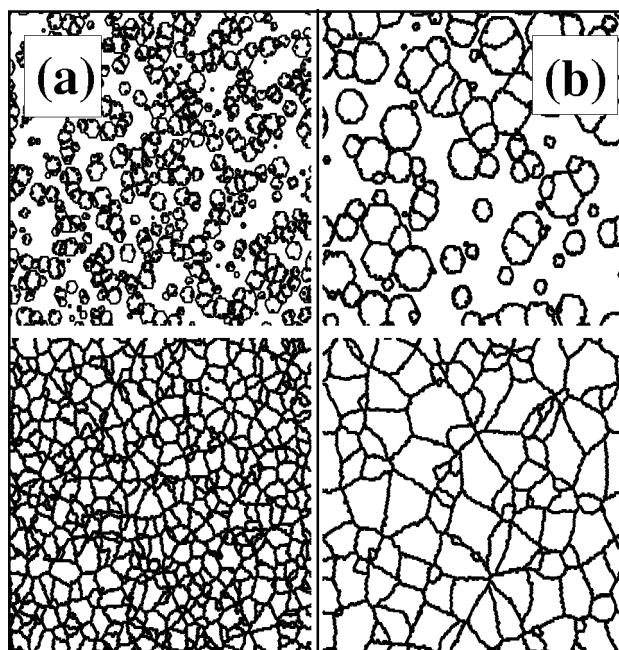


FIG. 1. Computer simulation obtained for two stages of the transformation process on a 250×250 triangular lattice with (a) $c = 1$ (homogeneous nucleation), $n = 0.001$, and $g = 0.8$ (total run time, 1 s.); and (b) $c = 0.1$, $n = 0.001$, and $g = 0.8$ (total run time, 1 s).

of c , which would in principle mean that growth is by site saturation, low values of n (large energy barriers for nucleation) lead to $m \approx 3$, as in continuous nucleation.

Other forms of experimental behavior lead to the occurrence of nonstraight KJMA plots. We argue that this fact may be due, on the one hand, to the decay of the nucleation rate when $n \ll 1$, because some potential sites are overlapped by already growing grains; and on the other hand, when the potential site concentration is $c \ll 1$, the grains grow independently for times lower than a characteristic impingement time, proportional to the mean grain distance $1/c^{1/2}$. Figure 2 shows this fact for several choices of parameters n and c . Note that when $n \leq 1$, the potential sites nucleate during the earlier stages of the transformation, so the mentioned overlapping of potential sites cannot be the cause of the bending of the KJMA plots. Therefore, we must conclude that heterogeneous nucleation is not the unique cause of the unexpected bending of the KJMA plots, as m may be affected by

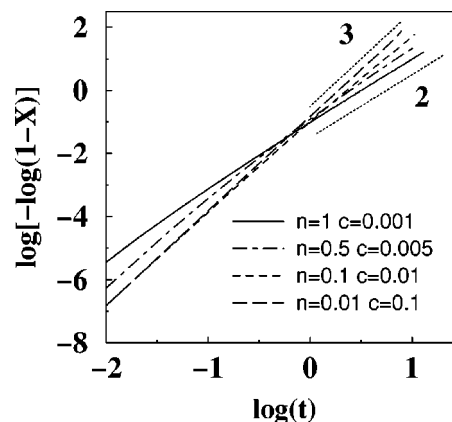


FIG. 2. KJMA plots for different sets of parameters. The dotted lines represent the theoretical slopes 2 and 3.

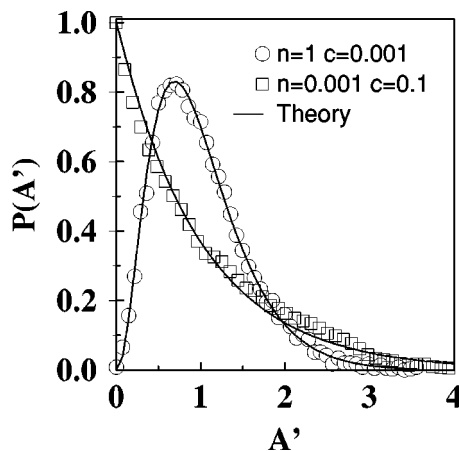


FIG. 3. Histograms of the grain-size distribution for different sets of parameters.

anisotropies or preferential crystalline directions yielding growth or nucleation rates that may change locally throughout the material. This agrees with the fact that m is not a reliable guide to characterize the morphology of the evolving grains.¹⁶

As we have pointed out, our model provides information about microstructure, i.e., number of grains, mean grain area, grain-size distribution, and so on. For site saturation, Weire, Kermode, and Wejchert proposed a *phenomenological* expression for grain-size distributions:¹⁷ $P(A') = (A')^{\alpha-1} \alpha^\alpha e^{-\alpha A'} / \Gamma(\alpha)$, where $\alpha \approx 3.65$ and $A' = A/\bar{A}$ is the reduced area. The mean area \bar{A} changes from one process to another, but the normalized distribution is the same for all. Analogously, in the case of continuous nucleation, a simple expression has been proposed:¹⁸ $P(A') = e^{-A'}$. Figure 3 shows the good agreement between the simulations of our model and these theoretical predictions. For intermediate-ranging parameters, a continuous evolution is obtained from site saturation to continuous nucleation grain-size distributions. We thus have two elements of comparison between our model and experimental results: the KJMA exponent m and the grain-size distribution $P(A')$.

In conclusion, we have presented a simple lattice model for crystallization which sheds light on the possible causes of the experimental deviations from the KJMA theory. Thus, preexisting inhomogeneities in the initial state, such as regions with a lesser degree of disorder or impurities, dramatically change the product structure and the time development of the crystalline phase. One of the remarkable points of our

model is its versatility, so other ingredients can be simply added to the model rules. We postpone the detailed study of heterogeneous growth or preferential directions to further research. The main conclusion of this work is that the KJMA exponent is not enough to understand and to characterize the crystallization mode in a specific experiment: Indeed, we have shown that conditions close to site saturation and continuous nucleation give rise to very similar values of m . Therefore, studies of the grain-size distribution are indispensable to identify correctly the crystallization mode. We stress that the model rules are physically meaningful (alternative proposals can be found in Ref. 19, but are far from being physical because they depend strongly on the lattice geometry and the site interactions), and lead to experimentally verifiable predictions. Due to its versatility and short simulation times, it is easy to reproduce a good and nonexpensive testbed for the design of materials and structures with tailored grain size or shape properties.

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