Fractal Aggregates in Sputter-Deposited $NbGe_2$ Films

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Fractal-like structures have been observed in sputter-deposited thin films of $NbGe_2$. These structures exhibit a striking resemblance to those produced by computer simulations of diffusion-limited aggregation using the Witten-Sander model. An effective fractal dimensionality of about 1.9 has been determined from digitized photomicrographs. Our results indicate a two-stage growth process in which an initial structure with a fractal dimensionality of about 1.7 is thickened by a subsequent growth process.

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Sputter deposition has come into use over the past twenty years as a major technique for preparing thin films for a variety of applications. Many materials and metastable phases not otherwise obtainable as thin films have been produced by this process. One of the major concerns with all thin films is the morphology of the surface, since it often strongly influences the electrical characteristics of devices made with such films.

Recently considerable interest has also developed in a wide variety of growth and aggregation models. This work was stimulated by the discovery by Witten and Sander[1] that a simple diffusion-limited aggregation model in which particles are added, one at a time, to a growing cluster of particles via random-walk trajectories leads to scale-invariant structures with a fractal dimensionality[2] (D) which is considerably smaller than the Euclidean dimensionality of the space in which the growth process is occurring. Two-dimensional simulations lead to structures with a fractal dimensionality of about 1.7.[2,3] This paper reports the existence of fractal-like structures on the surface of sputter-deposited $NbGe_2$ films and correlates their fractal dimensionality with the results of simulations to provide hypotheses for the growth mechanisms.

In 1978, a unique sputter-deposition process was developed at the Naval Research Laboratory to produce films of Nb_3Ge. This process initially produced films of $NbGe_2$ with a previously unobserved surface structure. Complex clusters were visible on the surface under an optical microscope at magnifications of a few hundred. Figure 1 shows a digitally reproduced image of a photomicrograph from one of these films. Changing the sputtering conditions to produce the desired material eliminated the surface features, and study of this phenomenon languished. Our interest in these systems was recently revived by the striking visual similarity between the surface structure found in the Nb-Ge thin films and pictures of two-dimensional simulations of diffusion-limited aggregation.[1,3,4] This led to the hope that information concerning the mechanisms which yielded the structures might be obtained from a more quantitative analysis.

The films were prepared by rf reactive sputtering of a niobium target in a mixture of argon and germane gases at pressures less than 100 mT. The quartz substrates were heated to 840 °C during deposition by a carbon-fiber-heated Mo table. The temperature was measured with an infrared pyrometer focused on the substrates prior to and immediately after sputtering. The films thus formed were 2000 to 5000 Å thick and consisted of a layer of small grains (average size about 0.1 μm) with larger grains (average size about 1 μm)

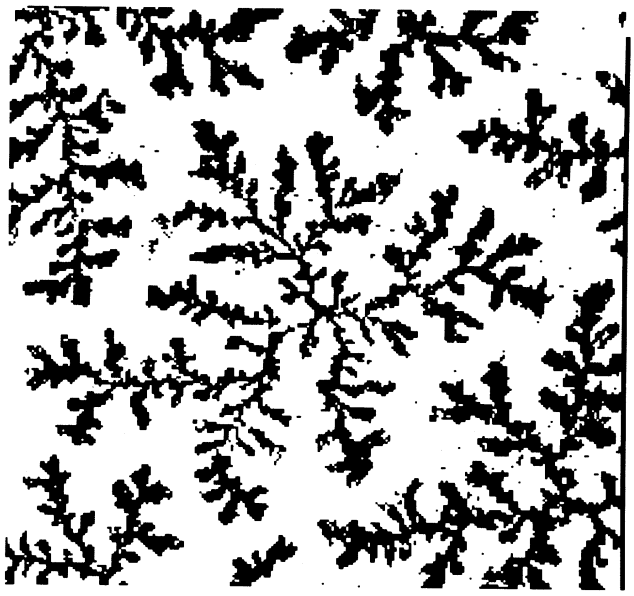

FIG. 1. A digitally reproduced photomicrograph (250×) of a cluster formation on sputter-deposited Nb-Ge thin film.

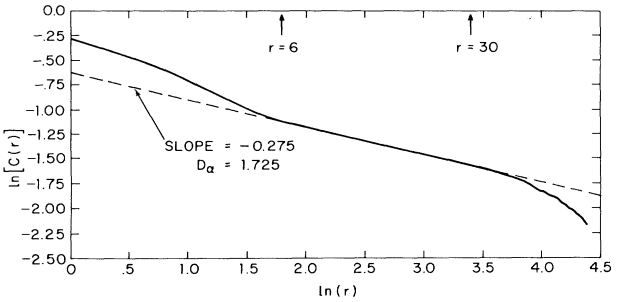

FIG. 2. Logarithmic plot of density-density correlation function vs radius. The solid line represents the average correlation from tracings of four clusters similar to that shown in Fig. 1. The tracings are constant width and eliminate the effects of thickening near the edges of the cluster. The dotted line is a least-squares fit from $r = 6$ to 30 pixels and corresponds to a fractal dimension of about 1.7.

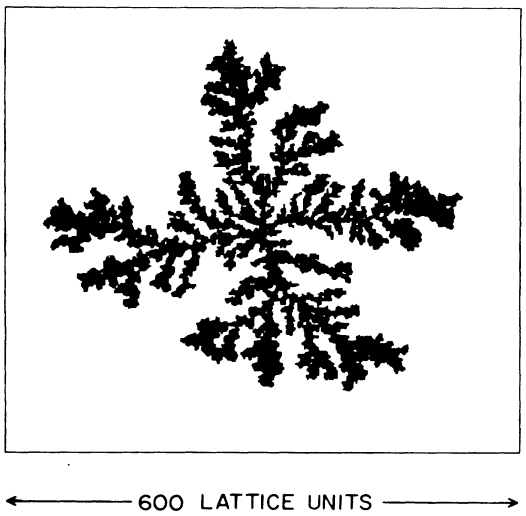

FIG. 3. Two-stage simulation using the Witten-Sander model. 10 000 particles were added with unit sticking probability followed by 15 000 particles with 0.1 sticking probability.

formed into the clusters on top. In the film with densely spaced, well developed clusters, the small-grained layer was uniform in appearance as judged both visually and via scanning electron microscopy. In the film with sparser, less well developed clusters, the electron micrographs showed numerous disjoint holes in the small-graining layer and what appeared to be larger grains aggregating from the material in some holes. The former film was made by constantly adding GeH_4, while the latter film was made at higher total pressure and with no GeH_4 added during the last half of the deposition. In neither case was the by-product hydrogen gas removed from the chamber during deposition. Recent x-ray fluorescence measurements were unable to detect any difference in the Nb-to-Ge ratio between the larger and smaller grains.

To make quantitative comparisons with simulation results, it was necessary to measure the fractal dimension of the structures. Photomicrographs taken of individual clusters were digitized using a Hammamatsu video camera at 256×256 resolution. A threshold criteria was then applied to separate pixels in the cluster from those in the background. Logarithmic plots of the number of such cluster pixels versus radius from the center of the cluster were made and the fractal dimension determined from the slope of these plots. The fractal dimension was also determined from the density-density correlation functions. The dense clusters, like those shown in Fig. 1, gave an effective fractal dimension of 1.88 ± 0.06. This was somewhat higher than expected and was attributed to the thickening of the outer limbs of the cluster. These limbs were "defoliated" by the simple expedient of tracing the centerline of each cluster limb with a thin-line pen. Digitized pictures of the tracings yielded an effective fractal dimension of 1.73 ± 0.08. This is indistinguishable within experimental error from the value of about 1.7 from computer simulations of diffusion-limited aggregation.[1,3] The more sparse cluster yielded an average fractal dimension of 1.69 ± 0.05, and lacked the thickening at the ends.

While clusters with a fractal dimensionality greater than 1.7 could be produced using Levy-flight trajectories,[5] they did not show the thickening evident in the experimental samples with dense clusters. The structure of the defoliated limbs, however, agreed very well with clusters produced by the Witten-Sander model for diffusion-limited aggregation. Figure 2 shows a plot of the density-density correlation functions obtained from averaging four of the tracings of defoliated experimental clusters.

Thickening can be achieved in the simulations by lowering the sticking probability. This allows the diffusing particles to explore more of the existing structure before attaching to it and thus fill the adjacent space to a greater extent. Since both the sparse clusters and the defoliated clusters agreed with simulated clusters grown with a unity sticking probability, a two-stage simulation was run to test the hypothesis that the thickening at the periphery could occur at a later growth stage. The first stage added 10 000 particles to a single seed on a 600×600 square lattice using single-step random trajectories and a sticking probability of 1. This produced a structure of constant thickness (about one lattice spacing) and a fractal dimension of about 1.7. For the second stage, 15 000 additional particles were added using a sticking probability of 0.1. The resulting cluster is shown in Fig. 3 and the agreement with Fig. 1 is apparent.

The above results suggest that growth of the dense

clusters can be separated into two stages. During the first stage, a narrow fractal structure with dimension of about 1.7 is formed. This provides the limbs upon which the final form grows. The two stages could be different physical mechanisms or they could be the same mechanism with a change in some parameter such as the sticking probability.

To see that the two contributions to our measurement of the fractal dimension are separable, assume that the thickness of the limbs increases with distance from the center according to some power law with exponent γ. If the Hausdorf dimension of the limbs, assuming zero thickness, is D, then the mass of just the limbs (M_l) as a function of distance from the center follows a power law with D as the exponent. Combining these dependencies gives the mass distribution of the whole cluster (M_c) as

$$M_c \propto r^{D+\gamma},$$

where now $D+\gamma$ is the "measured" or effective fractal dimension.

Further experimentation is underway to determine the details of the physical mechanism. The first question to be addressed is the relation between the simulation and the actual growth mechanisms. In particular, do the "particles" in the simulation correspond to the larger grains evident in the photomicrographs or to the newly arrived atoms or molecules? Aggregation of the grains is appealing because of the close analogy with the simulation and because of the existence of large grains in some holes and some isolated large grains in the less dense film. However, a mechanism for moving such large objects must be elucidated. Aggregation of atomic or molecular species is more physically plausible. Such a model would require an explanation for why the clusters are formed of large grains, especially ones larger than the base material. Kloska and Haase[6] report that in their coevaporated $NbGe_2$ films the grain size became highly nonuniform for deposition temperatures above 850 °C. Knoedler and Douglass[7] reported that their $NbGe_2$ films, sputtered from a $NbGe_2$ target onto a variety of substrates at temperatures less than 720 °C, show substantial surface superstructure which they characterize as "islands" of 2–10 μm in diameter.

A second question is the physical mechanisms underlying the two stages. An obvious possibility is the direct analogy of a physical decrease in sticking probability. Alternatively, a mechanism other than diffusion-limited aggregation could produce a structure with a fractal dimension of about 1.7 which would serve as a template for growth of the actual clusters. One possible candidate is a network of cracks or defects formed in the layer of base material due to thermal or other stresss. Such networks are only very speculative at present.

In summary, the information obtained so far has allowed an excellent start on understanding the mechanisms responsible for the patterns on the $NbGe_2$ sputtered films. When these patterns were first observed, they were considered intractable because they are random in nature. Measurements of quantities like the cluster mass as a function of distance from the center yielded quantitative information about the structure. The simulations of diffusion-limited aggregation provide a basis for interpreting the data on the fractal dimension of these clusters. The results strongly point to a two-stage growth process wherein during the first stage the limbs form with fractal dimension of about 1.7 on the surface of a layer of small grain material and during the second stage the limbs are preferentially thickened near the periphery. These results point the way toward further experiments to determine the details of the physical mechanisms responsible for the structures.

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