PHYSICAL REVIEW B VOLUME 40, NUMBER 4 1 AUGUST 1989

Discontinuously branching tree morphology induced at the NaCl/AgCo interface by ion irradiation

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(Received 16 May 1989)

We present a new class of fractal structure, discontinuously branching tree morphology (DBTM), developed at the NaCl/AgCo interface by ion irradiation. This kind of morphology is distinct from all the previous observed fractal patterns and cannot be explained by the diffusion-limited aggregation model. The observed DBTM's with fractal dimension of 1.56 have been proved to share many common features with lattice animals. Besides, many important aspects concerning pattern formation are also characterized in detail.

Fractal growth patterns, which manifest themselves in widely diverse fields,[1] have been extensively studied over the past few years. Most of the activity in this field has been based on computer simulation[2,3] and theoretical consideration.[4,5] Consequently, more detailed experiments have been seriously needed to uncover the essential points concerning the pattern formation.[6] Recently, there seems to be an increasing interest in studying the real-world patterns, and there have been several papers published on pattern formation in thin solid films.[7-11] Except for a few cases concerning a dense branching morphology (DBM),[10] most of these observed patterns can be compared to diffusion-limited aggregation (DLA),[2] which is believed to be the most successful model to capture the essential features of pattern formation.

In this Rapid Communication we present the observation of a new kind of fractal structure, for the first time, the discontinuously branching tree morphology (DBTM) induced at the NaCl/AgCo interface by ion irradiation. This sort of morphology with a fractal dimension of 1.56 ± 0.02 seems to have little coincidence with the DLA model, and cannot be classified as any previous observation. This notwithstanding, it is possible to compare the DBTM patterns with lattice animals.

Specimens were prepared by depositing alternatively pure silver and pure cobalt onto cleaved NaCl single crystals at room temperature. The vacuum level during deposition was better than 2×10^{-6} Torr. The thickness of the multilayers (about 200 Å in total) was designed to match the depth of the maximum damage density of the incident 180-keV xenon ions in the $Ag_{40}Co_{60}$ alloy films. In this case, the projected range of the irradiation ions was about 270 Å, meaning the ions could penetrate through the AgCo layers and thus resulted in mixing between Ag and Co layers as well as intermixing of AgCo and NaCl. The thickness of the outermost Co layer was increased by 50 Å in order to allow for the sputtering effect. The as-deposited films were then irradiated to the doses of 1×10^{16} and 3×10^{16} Xe atoms/cm^2. The target was water cooled and the ion flux was maintained at less then 4 μA/cm^2 to avoid significant heating of the specimens. The vacuum lever during irradiation was better than 5×10^{-6} Torr. After ion irradiation, some Na and Cl atoms were injected into the AgCo films through the interface, and the unmixed NaCl substrates were later dissolved in deionized water. The self-supported AgCo films were then put onto the Cu grids for transmission electron microscopy (JEOL TEM 200CX) examination. Selected area diffraction (SAD) and *in situ* energy dispersive spectroscopy (EDS) were also used to characterize the microstructures observed in the films.

Transmission electron microscopy bright-field examinations revealed that there were many discontinuously branching tree morphologies scattered in the ion-irradiated films (shown typically in Figs. 1 and 4). Unlike the ion-irradiated films, the as-deposited ones were homogeneous in morphology without any pattern and consisted of only polycrystalline silver and cobalt.

Figure 1 is a typical example of the ion-induced discontinuously branching tree morphologies observed in the film after irradiating to a dose of 1×10^{16} Xe atoms/cm^2. The ramified morphology with average size of 100 μm is composed of 0.2–1.0-μm particles with dark appearance, that generally line up in particular ways. There are also many flowerlike clusters located on the branches of the tree, and a great many smaller particles (0.05–0.1 μm) distributed randomly in the open area. From the density of the distribution of these smaller particles, it is clearly shown that there exists a screening field around the ramified branches. In order to unravel the self-similar feature of this sort of pattern, the electron micrograph in Fig. 1 was digitized with a VAX-M'750 image processor at 512×512 pixels resolution. The details of calculating the fractal dimension can be found in our previous publication.[8] The fractal dimension measured for Fig. 1 is $D = 1.56 \pm 0.02$, which reveals the scale invariance of this new kind of discontinuously branching tree morphology. Apparently, the dimensionality of 1.56 is much lower than

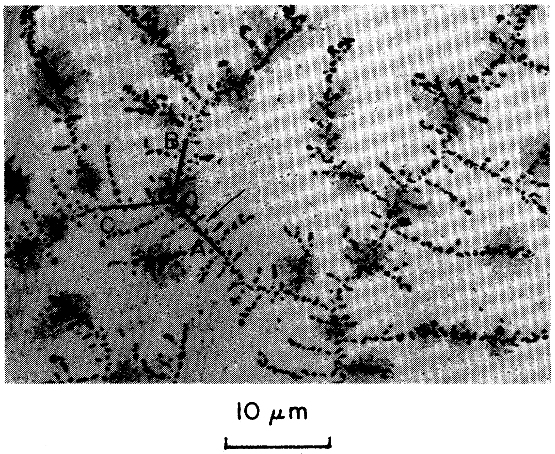

FIG. 1. A self-similar discontinuously branching tree morphology induced at the NaCl/AgCo interface by ion irradiation to a dose of 1×10^{16} Xe atoms/cm^2. The fractal dimension of this pattern is 1.56 ± 0.02. The line segments *OA*, *OB*, and *OC* show clearly the bifurcation angles among these three main branches.

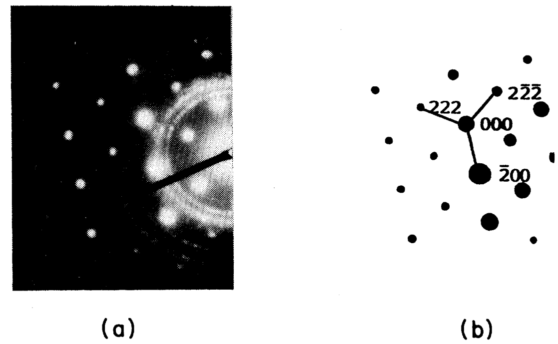

FIG. 2. (a) Electron diffraction pattern taken from the arrowed particle on the branch *OA* shown in Fig. 1. The diffraction lines come from the background composed of polycrystalline Ag and α-Co. The diffraction spots show that each dark particle (because the orientation of the NaCl single crystal meets the need of Bragg diffraction, the intensity of electron beam after passing NaCl reduced a lot, resulting in a dark appearance) is one NaCl single crystal. (b) Indexing results of the diffraction spots in (a) showing that the angles in fcc lattice among crystallographic directions [100], [111], and [111] lying in the film plane exactly equal to the bifurcation angles labeled in Fig. 1.

the 1.67 predicted by the DLA model,[2] yet it is nearly the same as that calculated by the two-dimensional lattice animals.[12]

The composition of the background was determined by EDS to be approximately $Ag_{30}Co_{65}Cl_5$, and at the dark branches there are additional 15% Na and 15% Cl. It indicates that the discontinuous branches consist of NaCl precipitates. The elements Na and Cl resulted from the interfacial mixing which injected Na and Cl atoms into the AgCo overlayer by irradiation enhanced diffusion and recoiling mixing.[13]

For one of the particles arrowed in Fig. 1, sharp diffraction spots are shown in Fig. 2(a) [also indexed in Fig. 2(b)], which confirm that each precipitated NaCl particle is one single crystal. The diffraction rings arise from the polycrystalline silver and α-cobalt. Figure 3 is a magnified bright image taken from Fig. 1 which shows the relationship between the tree branches and its flowers. It is also indicated that the multilayered AgCo films were homogeneously mixed up and had very fine crystalline grain structures with a linear size of about 200 Å, which would provide enormous grain boundaries to allow the small atoms of Na and Cl to diffuse through.

By scrutinizing Fig. 1, one can find another profound characteristic that governed the way in which the pattern was organized. The tree branches, formed by lining up the single-crystal NaCl particles, randomly bifurcate into some specific angles such as 90°, 60°, 30°, etc. For instance, at the bifurcation point labeled by *O*, there are three main branches *OA*, *OB*, and *OC* crossed; the angles between these branches were easily measured to be $AOB=AOC=125°$ and $BOC=110°$. Figure 2(a) was taken from one of the particles on the *OA* branch. According to the indexing results shown in Fig. 2(b), it is clearly seen that the angles in fcc lattice among crystallographic directions [100], [111], and [111] lying in the film plane were $[100]\wedge[111]=125.3°$, $[100]\wedge[111]=125.3°$, $[111]\wedge[111]=109.5°$, which are remarkably in agreement with the above bifurcation angles among the *OA*, *OB*, and *OC* branches. The way of bifurcation, therefore, seems to reveal the underlying in-plane symmetry of fcc NaCl lattice. The particle spacings (around 0.5 μm) are therefore thought to make it possible for branches to bifurcate randomly in some intrinsic angles.

When the dose went up to 3×10^{16} Xe atoms/cm^2, another sort of morphology is displayed in the films, as shown in Fig. 4, which is more anisotropic than that in Fig. 1 and vividly shows the two-dimensional (2D) tree morphology. Correspondingly, no unique fractal dimension can match this kind of pattern. However, it has been

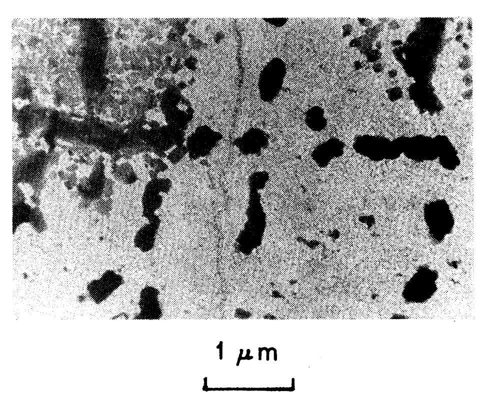

FIG. 3. A magnified bright-field image taken from Fig. 1, showing evidently the relationship of the branches and their flowers, also indicating a large amount of grain boundaries.

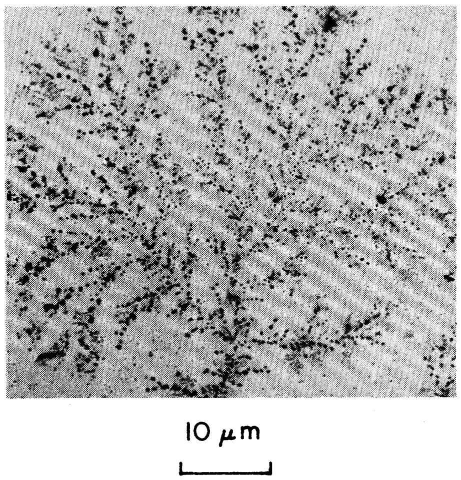

FIG. 4. Another sort of two-dimensional tree morphology with no unique fractal dimension appearing in the films when a dose went up to 3×10^{16} Xe atoms/cm^2.

figured out that the pattern shown in Fig. 4 is a typical example of the multifractal growth, and a further analysis of the multifractality is now being undertaken.

It is well known that Ag and Co are immiscible even in the liquid state. The heat of formation for the Ag-Co system is about +11 kJ/mol,[14] whereas the standard heats of formation[15] of the compounds NaCl, $CoCl_2$, and AgCl are −411.0, −325.5, and −127.0 kJ/mol, respectively. Obviously, Na and Cl atoms have the largest affinity and possibility to bond together. This is why we have chosen NaCl in our experiment, and is probably the reason why the tree branches are only composed of NaCl single crystals, but not otherwise. Presumably, the flowers shown in Fig. 1 may be mainly composed of $CoCl_2$ clusters. Similar to the argument made by Hou and Wu,[11] the large amount of heat released by combining of Na and Cl is also thought to affect the pattern formation considerably.

By analyzing a few examples of pattern formation in the thin solid films,[8-11] one will find that the homogeneous and isotropic background, such as the amorphous matrix, seems to be a necessary condition for the patterns, especially the fractal patterns, to grow. In our case, however, the polycrystalline background is much more anisotropic than the amorphous cases in microscopic structure. An anisotropic matrix together with the pattern elements (stronger anisotropy single-crystal NaCl) will certainly result in an anisotropic morphology, which is more evident in Fig. 4. Polycrystalline phase with fine structure and defects produced by ion bombardment would initiate heterogeneous nucleation of NaCl easily. It will partially account for the discontinuity or the multiple fixed points for diffusion which is quite distinct from the case of DLA having only one fixed point. Another factor leading to discontinuity of branches should be attributed to the possible increase of energy between two mismatched lattices. This acts as a repulsive force between the two neighboring single-crystal particles.

From the above, the discontinuously branching tree morphology in the first case has a self-similar structure with a fractal dimension of $D=1.56$, which matches the value predicted by lattice animals very well. Lattice animals represent the statistics of clusters in an equilibrium model away from the critical point,[16] which has become an interesting subject because of its applications in many diverse fields including clustering and nucleation,[17-19] spinodal decomposition, and dilute branched polymers.[20]

In addition to the same fractal dimension, the discontinuously branching tree morphology in Fig. 1 does resemble the lattice animals in some other aspects. First of all, the separate single-crystal particles generally line up in a chain with nearly constant spacings to form a tree branch, and the whole pattern looks similar to a 2D dilute branched polymer. Secondly, as mentioned above, the crossed branches usually form some intrinsic angles possessed by the fcc lattice. As a consequence, these single-crystal particles can be regarded as the animals located in some lattice. Furthermore, the anisotropic shape of our observed tree morphologies is also in accordance with the theoretical prediction made by Family, Vicsek, and Meakin[16] for the large two-dimensional lattice animals.

In conclusion, we have presented a new class of fractal structure, namely DBTM, produced in thin solid films by the ion beam method, elucidated some static features of this new kind morphology, and, especially, succeeded in matching the fractal tree patterns to the lattice animals. It is worthwhile to mention that similar phenomena have also been observed by our group.[21] However, the exact physics responsible for the formation of this kind of fractal structure needs much more study. Recently, we have developed a cascade nucleation model for approaching a better understanding of the formation mechanism, and the results will be published in a forthcoming paper.

We are grateful to Professor K. Tao and Professor Y. H. Wang for stimulating discussions, and to Dr. J. M. Palmer for critical reading of the manuscript. We would like to acknowledge the staffs of the TEM Laboratory of Beijing University and the staffs of Analysis Center and Image Center of Tsinghua University for their help. We also acknowledge partial financial support from the National Natural Science Foundation of China as well as from the International Atomic Energy Agency (Research Contract No. 4731/RB).

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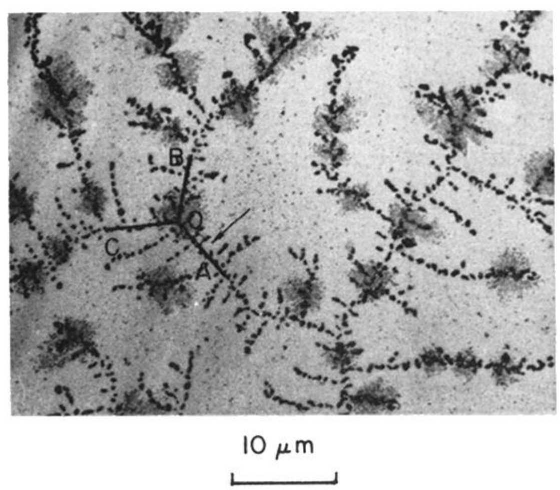

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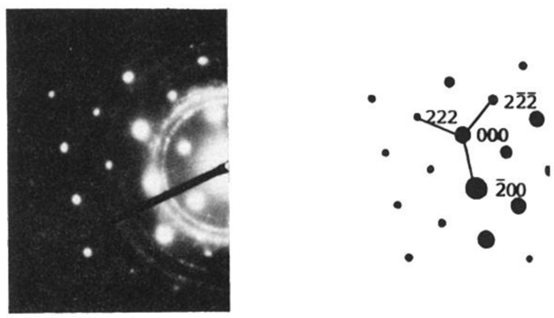
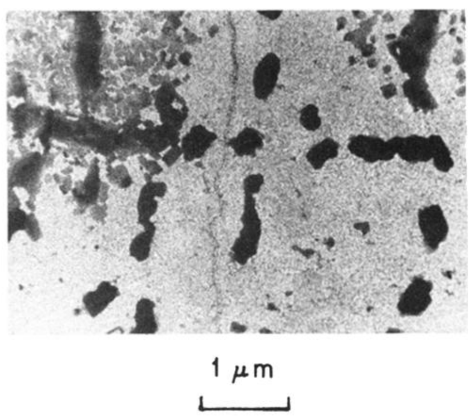


(a) (b)

FIG. 2. (a) Electron diffraction pattern taken from the arrowed particle on the branch *OA* shown in Fig. 1. The diffraction lines come from the background composed of polycrystalline Ag and α-Co. The diffraction spots show that each dark particle (because the orientation of the NaCl single crystal meets the need of Bragg diffraction, the intensity of electron beam after passing NaCl reduced a lot, resulting in a dark appearance) is one NaCl single crystal. (b) Indexing results of the diffraction spots in (a) showing that the angles in fcc lattice among crystallographic directions [100], [111], and [111] lying in the film plane exactly equal to the bifurcation angles labeled in Fig. 1.



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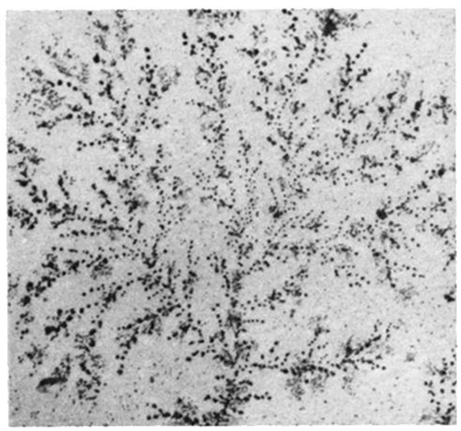

10 μm

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