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Fractal electrodeposits of silver and copper films induced by an organized monolayer

G. P. Luo, Z. M. Ai, J. J. Hawkes, Z. H. Lu, and Y. Wei
Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, 210018, People's Republic of China

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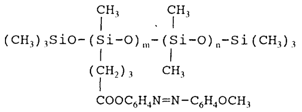
Electrodeposition experiments were carried out using silver nitrate or copper sulfate solutions ($AgNO_3$ and $CuSO_4$), with organized molecular films at the interface of the solutions. We found that the two-dimensional silver films have a fractal transition boundary which grows outwards when a constant current is applied while for copper films a space-filling fractal structure grows within the film's current boundary when a constant voltage is applied. The kinetics of the film growth is described and a model is given to explain the fractal growth of silver films. Some results for two-dimensional fractal deposition of copper in the absence of monolayers are also reported.

Electrochemical deposition of copper and zinc has been widely studied in the past decade.[1–13] These investigations were prompted by the development of the diffusion-limited aggregation (DLA) model.[14] In early experiments, some authors used *n*-butyl acetate as the interface of the metal sulfate solution and they obtained two-dimensional zinc metal leaves with an intricately branched random pattern.[2] In later work,[3,4] much thinner cells were used to approximate two-dimensional space; dendritic and disordered patterns as well as the DLA-like growth were observed by changing the parameters. Unfortunately, there have been few reports[15] about the fractal growth of silver leaves or films. In this paper, we will report some fractal phenomena in the growth of silver and copper films induced by organized monolayers. We show that two-dimensional silver films can have a fractal transition boundary when a constant current is applied and the internal morphology of the copper films can grow with a fractal structure. A kinetic model is given to explain the fractal boundary of the silver films while a hypothesis is presented to suggest why copper films have internal fractal growth. Further questions are raised by the growth patterns of copper leaves deposited without monolayers described at the end of this paper.

The experimental apparatus consists of a petri dish of diameter 9 cm and 1 cm high filled with silver nitrate ($AgNO_3$) or copper sulfate ($CuSo_4$) solution to a depth of 3 mm, onto which the polymer liquid crystal with the following formula:



$$(CH_3)_3SiO-(Si(CH_3)((CH_2)_3COOC_6H_4N{=}N-C_6H_4OCH_3)-O)_m-(Si(CH_3)(CH_3)-O)_n-Si(CH_3)_3$$

is poured to make an organized monolayer. The surface of the solution was cleaned with a water aspirator just prior to monolayer spreading. About 20 μl (0.001 M, dissolved in chloroform) amount of the spreading solution was carefully injected into the cleaned aqueous surface to form 20 Å/molecular monolayer from the polymer liquid crystal. The anode was either a silver or copper ring of diameter 8 cm (5 mm high and 0.5 mm thick) and was placed in the petri dish; the cathode was a platinum needle with a tip of 0.1 mm that was held upright at the center of the anode ring by a micromanipulator which controlled its vertical movement.

The electrochemical deposition at the electrodes of a cell has almost always been studied with constant applied voltage for people intended to mimic the electrochemical analog of the DLA process.[12] To grow silver films in negatively charged organized monolayers, polymer liquid crystal, we also used a constant dc potential and we obtained two-dimensional silver films (shown in Fig. 1). Similar films have been obtained by Zhao and Fendler.[15] The current through the cell increases with time, and when the applied voltage is constant the velocity of the growth is almost stable. This leads to the formation not having a transition structure, although the film grows larger and larger along the negatively charged interface of the solution. By changing to a constant current, rather than a constant voltage, to grow the film we have observed a transition with fractal structure surrounding the boundary of the dense two-dimensional film. Figure 2(a) shows the pattern of the silver film under polymer liquid crystal monolayer when the current begins at 0.13 mA ($C = 0.01$ M). The velocity of the growth falls after an initial 5-min period of fast growth. The potential voltage of the cell also decreased from 1.0 V to around 0.4–0.5 V,

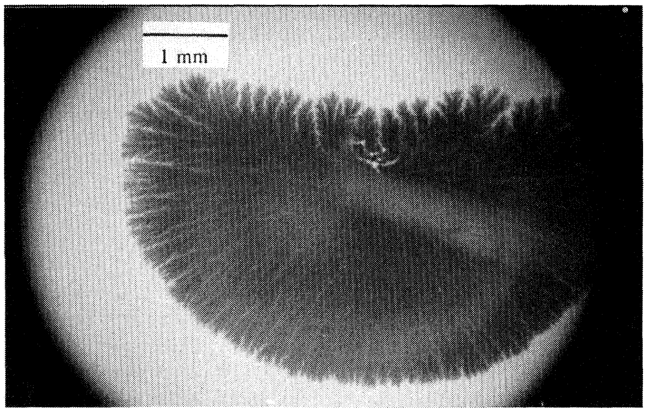


FIG. 1. Two-dimensional silver films deposited under a monolayer at a constant applied voltage ($C = 0.01$ M, $V = 0.82$ V).

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close to the electrode voltage of silver nitrate solution. By use of a microscope, we found the silver was two-dimensional with a fractal boundary. To obtain a larger film, we increased the current to 0.151 mA; the renewed growth along the boundary of the film was not even. Instead, superiority growth protruded from the old boundary in two-dimensional fanlike formations. This growth seemed to stop after a period of time and the voltage again decreased to about 0.4–0.5 V. We then increased the current to 0.17 mA and a similar phenomenon of the growth was observed, but at this time, the film was larger than before and less dense. After the two-dimensional growth almost stopped, we observed a slower growth of branches in a treelike formation [shown as the outermost in Fig. 2(a)]. The scale invariance was tested by computing the density-density correlation function for the digitalized patterns of the photographs. Its Hausdurff dimension average over many points in Fig. 2(b) is $D_f = 1.52 \pm 0.02$ [shown in Fig. 2(c)].

The experiment shown above has been simulated by computer using the DLA model. In the absence of a field, the DLA model describes a pure random walk on a square lattice, the probability of one particle moving from position i to an adjacent position j is $\frac{1}{4}$. In the electronic field of our experiment, such a probability can be expressed as

$$P_{ij} = \tfrac{1}{4} + K(\varphi_i - \varphi_j) ,$$

where K represents the coherent coefficient of the field and where φ_i and φ_j are the potentials at position i and j, respectively. When $\varphi_i = \varphi_j$, since that is in the case that no electric field exists, P_{ij} reduced to $\frac{1}{4}$ as in the original DLA model.

If the electric field is uniform over the whole range, then P_{ij} can be expressed as [shown in Fig. 3(a)]

$$P_{ia} = \tfrac{1}{4} + K \cos\theta ,$$

$$P_{ib} = \tfrac{1}{4} + K \sin\theta ,$$

$$P_{ic} = \tfrac{1}{4} - K \cos\theta ,$$

$$P_{id} = \tfrac{1}{4} - K \sin\theta ,$$

where θ is the angle of vector **i**. Obviously $P_{ia} + P_{ib} + P_{ic} + P_{id} = 1$.

The growth process described in the last section can be treated as two steps. In the first step, the electric field is relatively strong which means the voltage through the cell is larger than the electrode voltage of silver nitrate, and in the second step, the electric field is very weak with

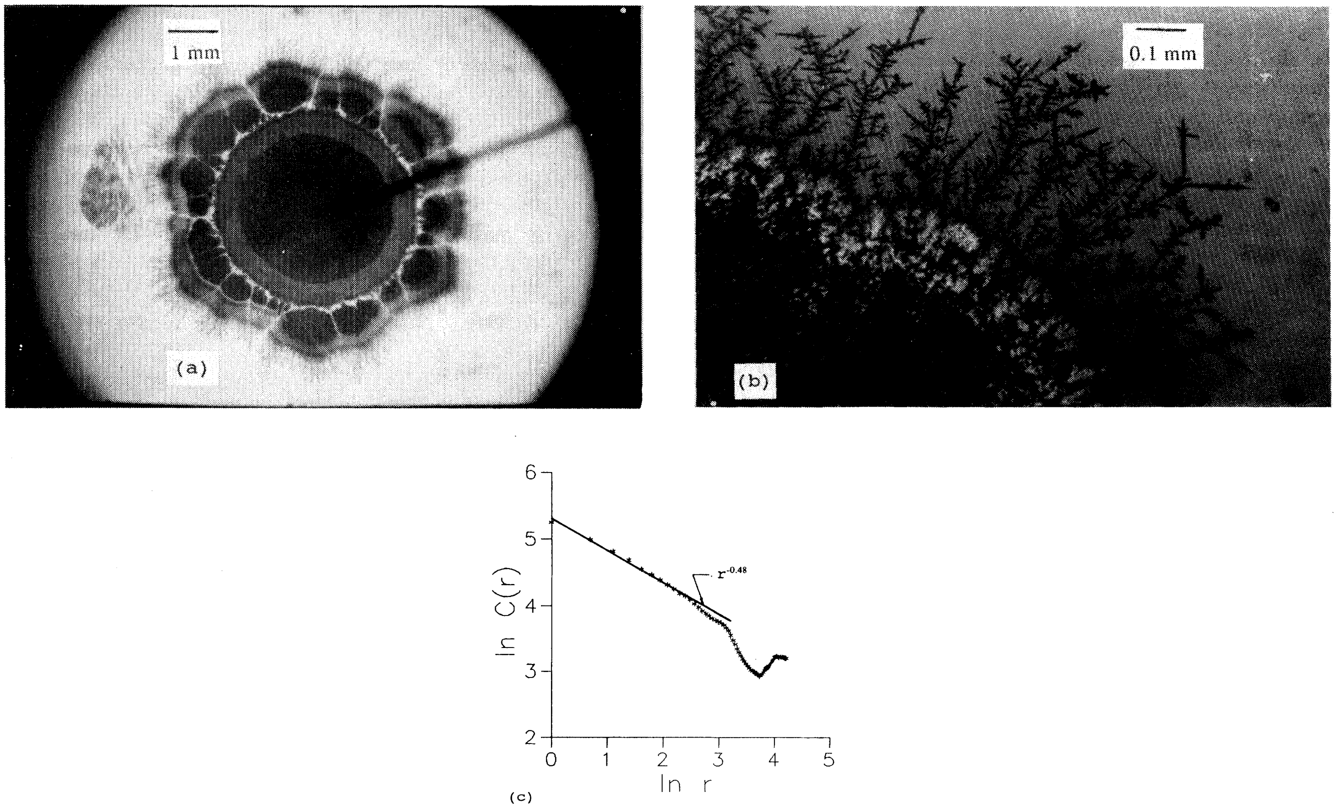

FIG. 2. (a) Full formation of silver film deposited along the monolayer (polymer liquid crystal) by a constant current (I changes from 0.13A to 0.171 mA, $C = 0.01$ M). (b) Open boundary of silver film shown in (a). (c) Density-density correlation function obtained by digitizing the photo of the metal leaf shown in (b). The exponent A obtained from the linear of $C(r)$ in this case is $A = 0.48$, which yields the fractal dimension $D_f = 1.52$.

$K=0$. According to the above quotation of P_{ij}, K should be controlled from $\frac{3}{4}$ to 0.

Using this model, the growth process has been simulated on a computer. Initially, K is set to 0.2 and then decreases to 0.1 a certain time later when the silver particles have been aggregated with dense structure. K is reduced to 0, which means the electric field is very weak (around to the electrode voltage). The result is shown in Fig. 3(b). We can see that a transition happens in the growth and the morphology is similar to that of the real growth shown in Fig. 2(a).

The density-density correlation function of Fig. 3(b) was tested by computer and the dimension of the boundary averaged over many points is $D=1.53\pm0.02$ [shown in Fig. 3(c)], which is in excellent agreement with that of the D_f from the real growth.

To study the growth of copper films through an organized monolayer, we again used a constant current applied to the cell but failed to obtain two-dimensional copper films; the copper was deposited only slowly and in three-dimensional rather than along the interface. We overcame the problem by using a constant potential in the range 0.5–10 V. A polymer liquid crystal was used to form an organized monolayer with the Langmuir-Blodgett (LB) technique.[15] A good copper film was produced with some fractal structure [see Fig. 4(a)]. The first band was grown at 0.7 V. Here copper aggregated slowly along the interface with high density and was two dimensional with a deep red color. After half an hour, the outward growth seemed to stop and the film became thicker and thicker. On increasing the voltage to 1.7 V, a renewed outward growth occurred at a high speed in two dimensions but under the interface. The new film was light green in color. The velocity of the deposition slowed down after a period of 10 min. As this happened a new density boundary formed with a deep red color, and the formation of the light green copper film changed from an even two-dimensional structure to a fractal aggregated structure [the outmost in Fig. 4(a)]. The particles of copper continued to grow larger until they sank to the bottom several hours later [shown in Fig. 4(b)].

The internal growth of the copper film radiated from the inside boundary of the film with treelike patterns. The branches are most numerous near the boundary line

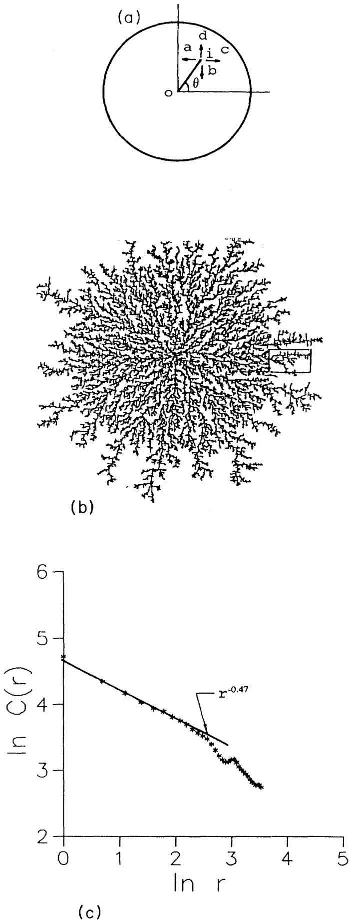

FIG. 3. (a) The calculation of the probability of one particle moving from position i to an adjacent position. (b) Simulation result by computer using DLA model. (c) Density-density correlation function from Fig. 4(a). The exponent $A=0.47$, which yields the fractal dimension $D=1.53$.

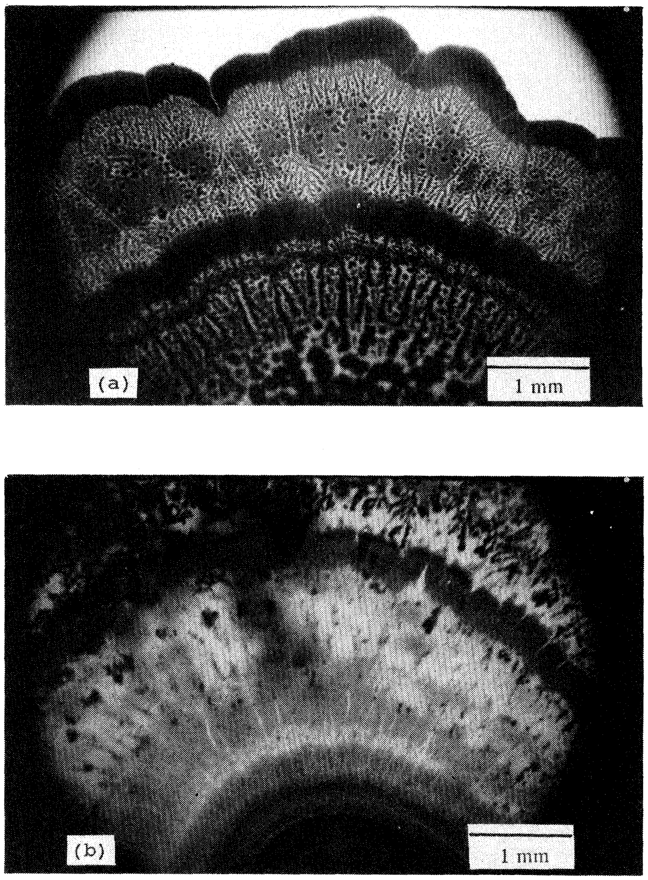

FIG. 4. (a) Two-dimensional copper film under polymer liquid crystal monolayer with internal fractal structure ($C=0.1$ M, $V=0.51-1.0-2.5$ V). (b) Aggregation of the film shown in (a) (2 h after stop deposition).

where they consist of many small copper particles. After several hours, almost all the internal copper aggregates into treelike patterns. By increasing the potential voltage again (to 2.5 V, for example) the same phenomenon will be observed again. Even though the fractal dimension of the internal pattern can be estimated or calculated, the growth process cannot be fully explained because it is difficult to recognize whether the internal thin layer of copper thickens as the result of an aggregation of small particles to larger ones or a new deposition of copper from the sulfate solution below the film.

Why is it difficult for copper to grow with two-dimensional structure by applying a constant current? We think that copper is more active than silver and if the velocity of the deposition is too slow, copper will oxidize, which results in new deposition being stopped; instead of that, copper will deposit in three-dimensional space. When a constant voltage is applied copper can deposit

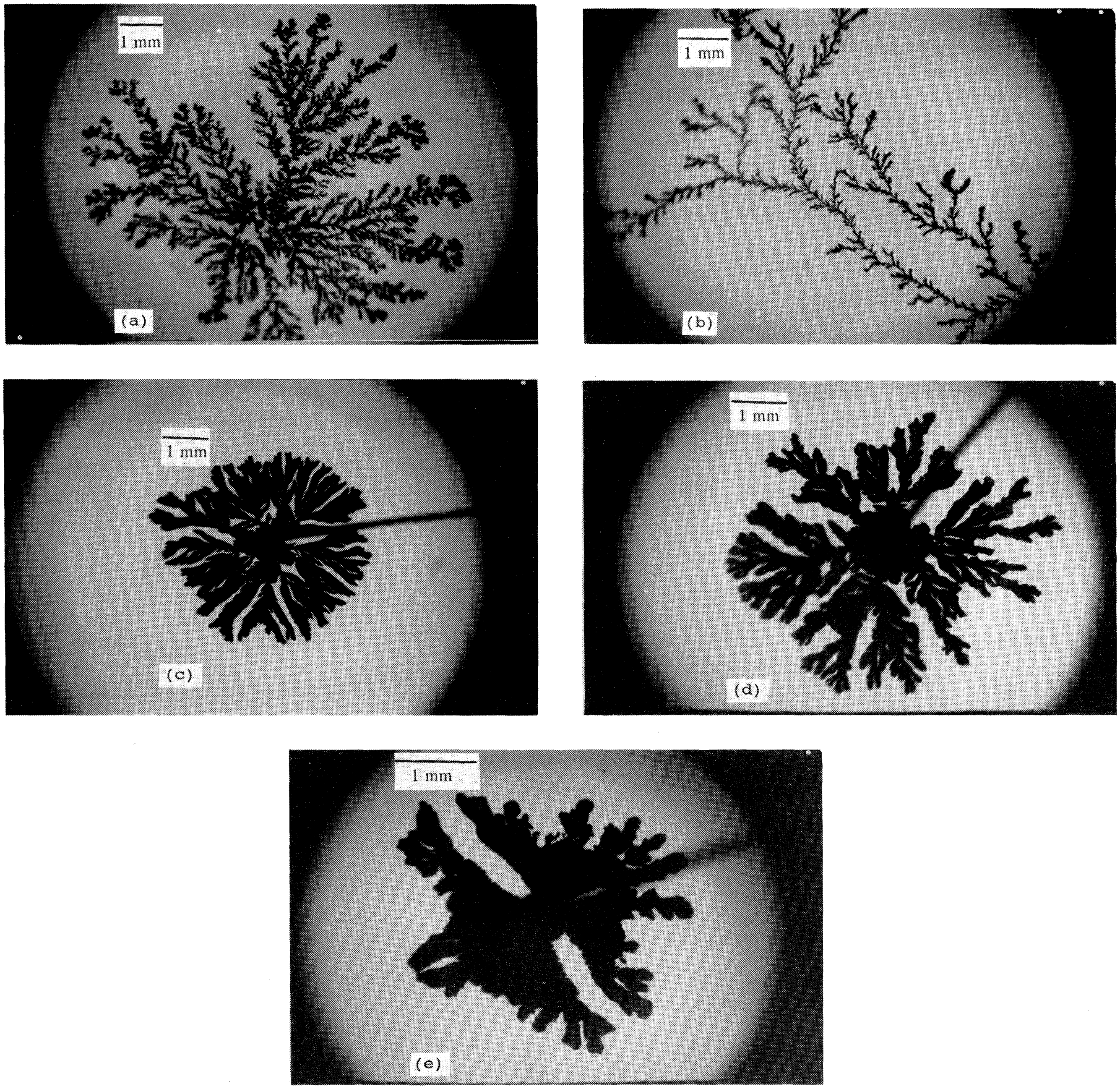

FIG. 5. (a) Three-dimensional open fractal DLA-like growth pattern ($C = 0.01$ M, $V = 1.7$ V). (b) Two-dimensional growth with string pattern ($C = 1.0$ M, $V = 7.4$ V). (c) Two-dimensional spokelike leaves pattern ($C = 0.25$ M, $V = 8.0$ V). (d) Two-dimensional growth with open ramified deposit ($C = 0.1$ M, $V = 4.9$ V). (e) Two-dimensional dense growth with open boundary ($C = 0.1$ M, $V = 1.7$ V).

with a certain velocity in two-dimensional space.

Using an organized monolayer, the interface of the solution is filled with negatively charged material which formed a stronger electric field. So silver or copper ions can deposit along the interface of the negatively charged layer. We can imagine that if the strength of the electric field is strong enough, it is easy to deposit metal ions. It is interesting to observe that the growth of copper leaves can also occur along the surface of the solution under certain conditions, namely when there are no monolayers on the solution.

Several kinds of growth were observed by changing the parameters (shown in Fig. 5). These patterns were selected from 30 photographs. Experiments were performed with the electrolyte concentration C ranging from 0.01 to 1.0 M and the applied potential difference V across the cell ranging from 0.7 to 10 V. Although four qualitatively distinct growth regimes were reported by Sawada, Dougherty, and Gollub, we are interested in another phenomenon of the growth described below. The solution in our cell is about 3 mm deep, compared to 0.1 mm used by other workers.[3,4] At low concentration (less than 0.02 M) and low V (less than 0.7 V) copper was deposited in a three-dimensional open DLA-like structure. An example is shown in Fig. 5(a). At higher concentration (0.1–1.0 M) and higher voltage (1.7–8.0 V) the leaves formed along the surface with different patterns [shown in Figs. 5(c)–5(e)]. Because the field is strong (from the cathode to the anode) and the concentration is higher, the field in the surface of the solution, where there is no material, is stronger than that in the solution since the cathode is just touching the surface, with the result that ions are easily deposited along the surface. Further experiments will be done to clarify the kinetics of the growth.

To conclude, a transition occurs in the electrochemical deposition of silver when a constant current is applied, and a negatively charged monolayer is used for silver to deposit in a two-dimensional structure. Under certain conditions, copper can grow along the interface of the solution in a fractal morphology although there are no monolayers on the surface.

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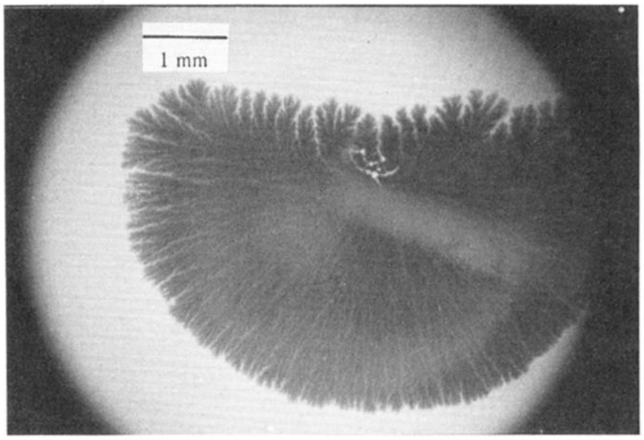

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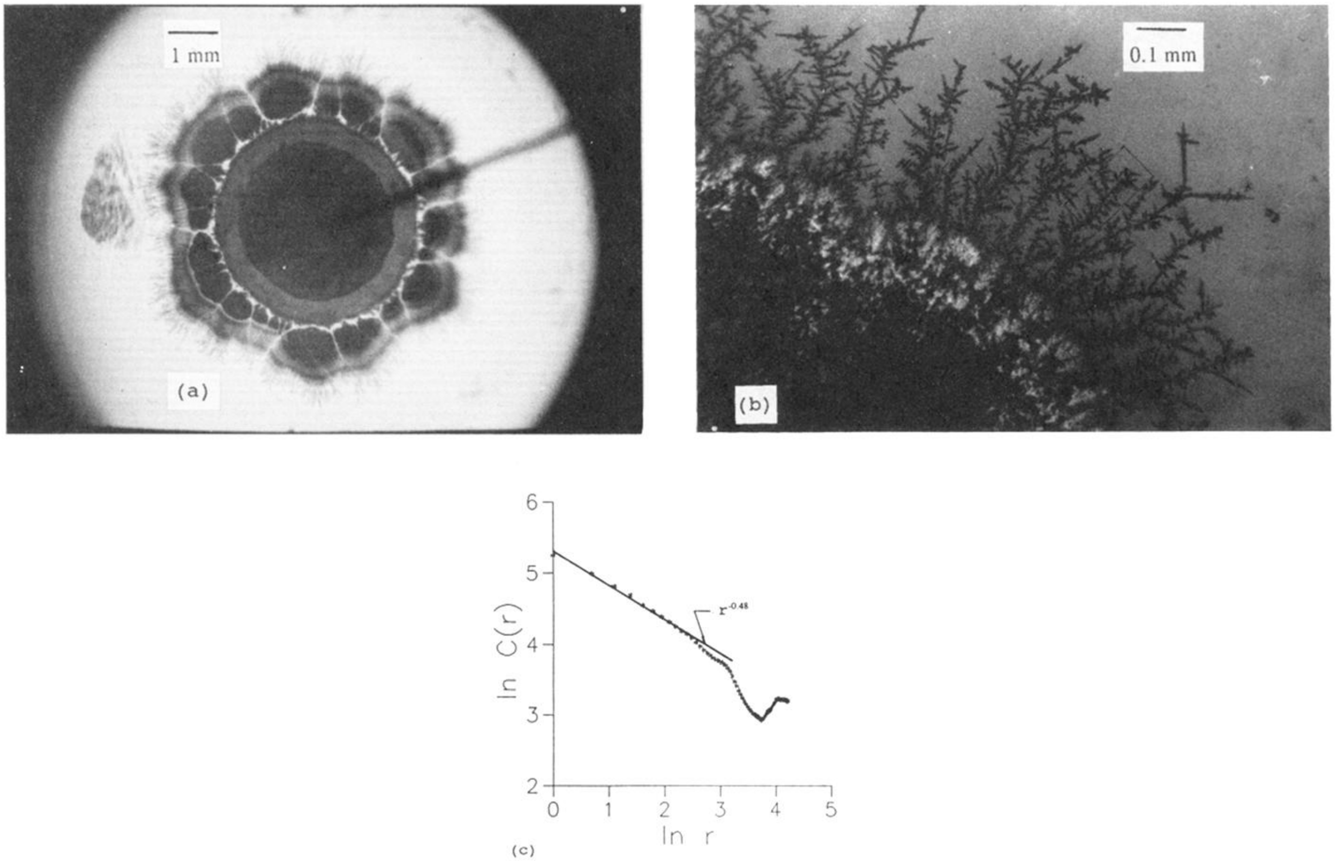

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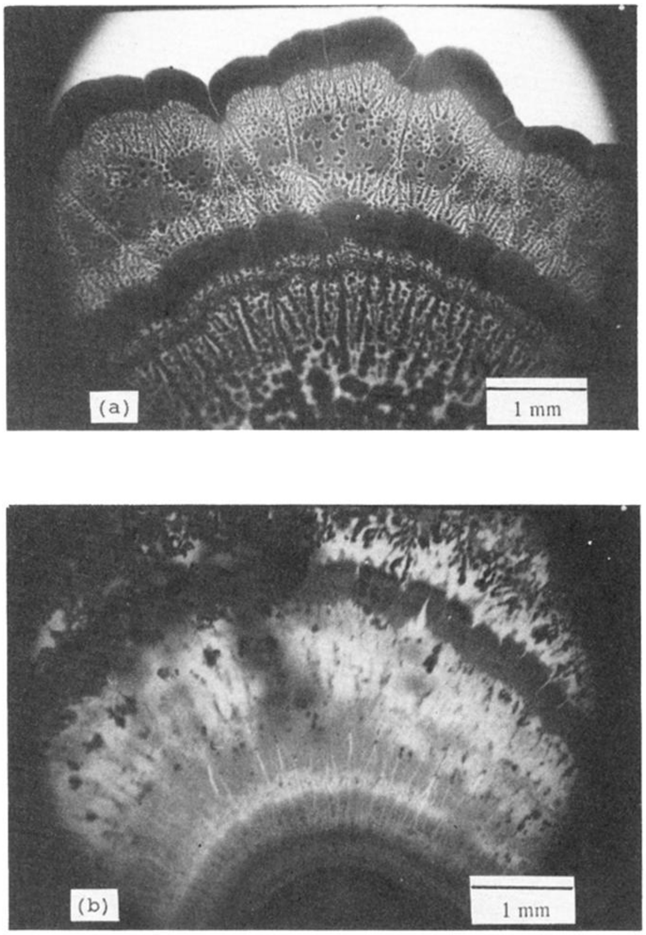

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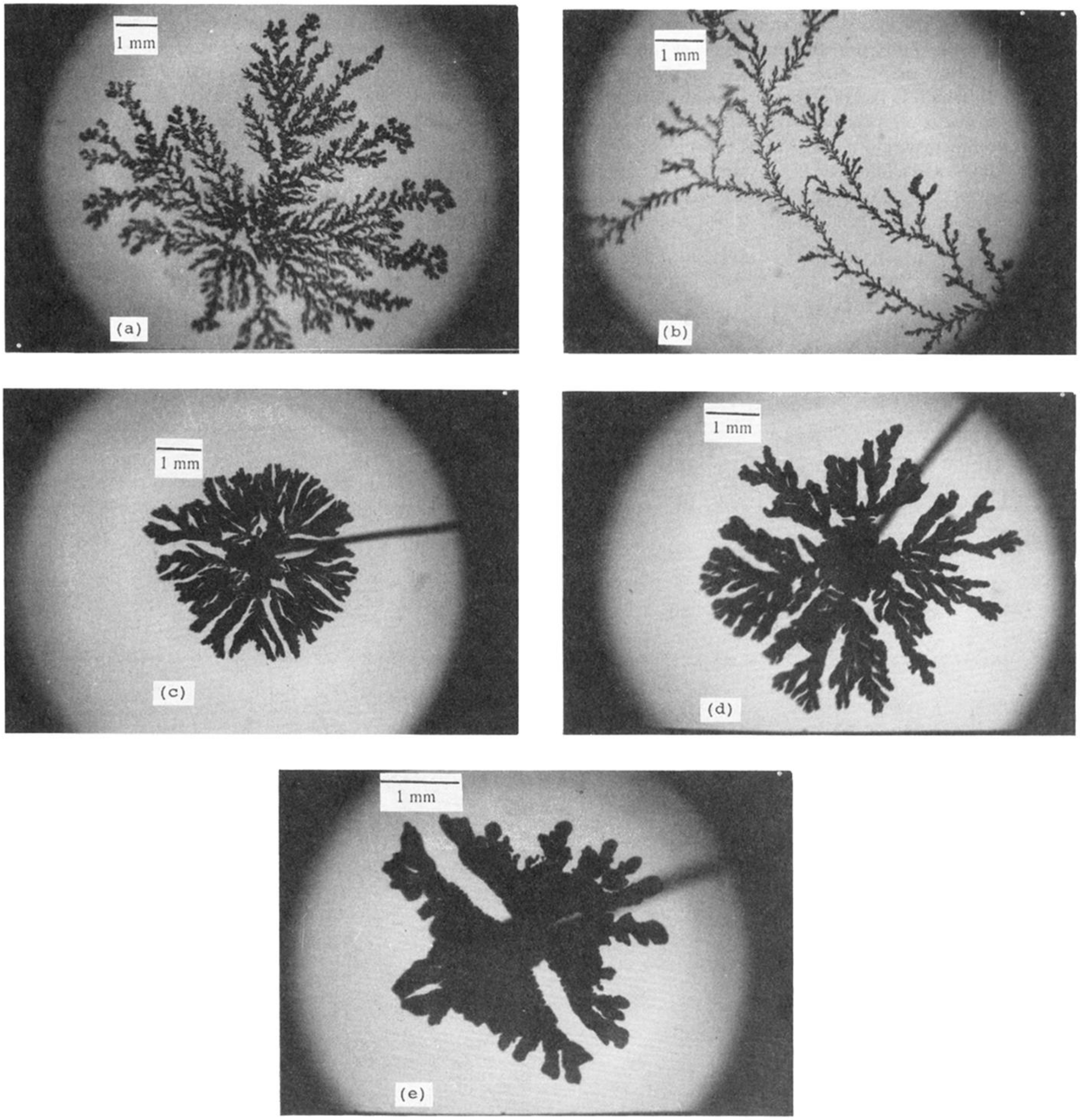

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