Dendritic Patterns Growth by Electro-Less Deposition Technique

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Abstract: We have studied and shown the dendritic pattrern growth of copper meatal using the technique of electro-less deposition. Unlike electro-deposition, in this technique the ions to walk toward the cathode (negative electrode) with required potential difference without cell applied voltage externally. The substrate used with the metals has developed the electric potential required for the migration of the metal ions to be deposited. Electro-less deposition cell was constructed by the deposition substrate is placed over the Aluminum plate and they are sandwiched between two glass plates. Dendritic pattern grown by preparing electrolyte at 1 molar concentration presented along with the fractal analysis of the patterns grown. The self-avoiding tendency is visible in the growth patterns due to the process of deposition are under DLA like conditions. The dendritic growth possesses self-similarity and scale invariance which is demonstrated using Log (N) versus Log(r) plot in box count technique and slope of this plot estimated the fractal dimensions are also discussed.

Keywords: Dendritic Patterns, Fractal Dimension, DLA, Electro-Less Deposition

I. INTRODUCTION

Dendritic patterns formation of metal ions in a small cavity in electro-less deposition technique showing scaling behavior and fractal characteristics under suitable operating conditions. The main process giving rise to such branching patterns is the Diffusion Limited Aggregation (DLA) [1, 2, 3] of ions under a week electric field. The patterns so obtained are also known as DLA patterns, this phenomenon is found to explain formation of many irregular shapes in nature. Diffusion controlled pattern formation have been recent topic of interest, amongst them the electro-deposition, viscous fingering, dendritic crystal growth, and DLA (Diffusion Limited Aggregation) have received the major attention. The concept of fractal and non-fractal aggregation is applicable in physics especially in turbulence [4, 5], polymerization, [6, 7]. Flocculation, coagulation, dendritic growth, crystallization. Gelation process also exhibit self-similarity and fractal character in many cases. The practical importance and fundamental principle of Diffusion limited growth processes has motivated extensive studies in the past years.

II. DESIGNING OF EXPERIMENTAL SET UP

Electro-less deposition cell was constructed by an Aluminum plate and the deposition substrate over it sandwiched between two glass plates. Cross sectional view of the electro-less deposition as shown in Fig.1, which is used during the experiments. The size of the plates used in the cell was 7.5 cm x 12.5 cm. High quality glass plates with surface finish were used during initial experiments settings, however latter it was realized that the surface quality of the glass plate was not among main parameter, therefore plane glass plates were used for remaining experiments.

III. METHODOLOGY

The experiment was setup by placing a paper of little larger size as that of the aluminum plate as a cell and pouring the electrolytic copper sulphate solution over it, to completely sopping the paper with a layer of electrolyte over it and sandwiched them between the two glass plates. As time

progress the solution flows from the sides while filling the cell and forms a thin layer between the aluminum plate and lower glass plate. It was found that this part of the solution has practically not played any role in the electro-less deposition; cause pitting of the aluminum plate from this side by way of chemical reaction. To maintain the plates in place the whole assembly was then clamped with paper clamps at four corners, two rubber bands were also used in some of the experiments and found to work satisfactorily.

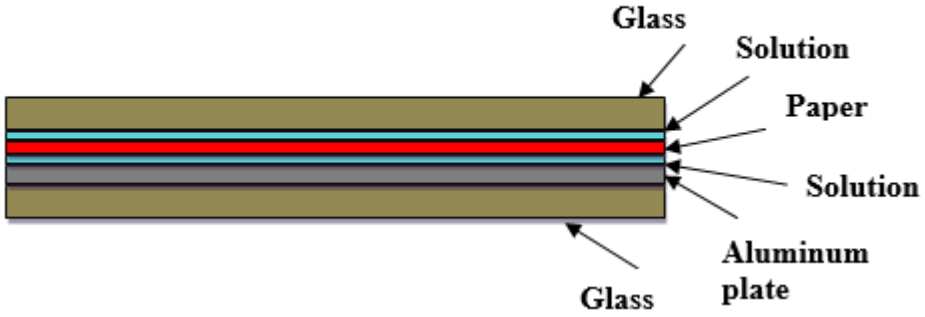

Fig.1: Design of electro-less deposition cell cavity

Nucleation process and time factor for governing deposits:

Since aluminum is electronegative with redox potential -1.66V and copper is electropositive with redox potential is + 0. 337 V so there is an exchange of aluminum ions with copper ions in copper sulphate solution. Copper gets deposited on aluminum plates and aluminum ions are released and a copper bridge is formed connecting aluminum plate with copper sulphate solution. There is formation of a nucleation center on the surface of a membrane [8]. The charge exchange between the copper ions and aluminum plate on the membrane surface takes place. Thus, initiating the process of Diffusion Limited Aggregation.

The clamped cell was filled with the electrolyte solution; and left open to air for 5 to 9 hours. Fine spots appear on the paper substrate approximately between 1-2 hours shows that nucleation begins. As time progress, these spots slowly grow in shape and size, some of them show slow growth and the others are found to be rapid in growth. It is observed that few of the spots grow in patterns, others into lumps and few of them result in beautiful dendritic patterns as shown in Fig.2a. It was also found that as compared to the rest of the portions, the growth is more common near the edges of the cell. As the time, elapsed healthy dendritic patterns were observed far away from the edges as shown in Fig.2b.

Figure: 2 (a). Showing lumps formation of copper metal deposits along with dendritic patterns

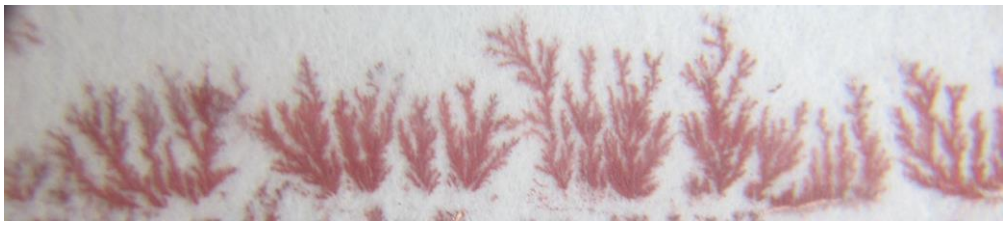

Figure: 2 (b). Showing electro-less deposition obtained with a 1 molar $CuSO_4$ solution in 8 hours

It is also observed that the texture of the growth pattern is little deformed as the photograph was taken after two or three days. This resulted in dislodging of branches of copper at the boundary of the deposit. A different deposit where most of the growth is dislodged is shown in Fig 3a. Electro-less deposition with dots and limited dendritic patterns under poor conditions is shown in Fig.3b.

(a) (b)

Figure:3 (a). Showing electro-less deposits with broken amorphous fragments
Figure:3 (b). Showing electro-less deposition with dots and limited dendritic patterns under poor conditions

Fractal dimension using box count technique:

Under best possible operating conditions few dendritic patterns grown are presented below. Electro-less deposition using a $CuSO_4$ solution having 1molar concentrations were used to obtain these dendritic patterns. The Electro-less depositions shown in Fig.4a is an original part of dendritic pattern grown on entire cell. The figure was first processed by changing its hue, saturation, contrast and brightness as shown in Fig.4b then converted it into monochrome image as shown in Fig.4c for analyzing self-similarity and fractal dimension.

In all the patterns, Box Counting Technique was implemented using a computer program written in Turbo Basic. The program identifies the size of the image in pixels and based on the image size, implements the box counting procedure by selecting suitable size of the boxes. For different size of boxes in pixels the effect on number of readings changes, also the points become very less crowded or more crowded as the number of pixels' changes. Starting with one pixel equal to the box side length, the program starts counting the number of boxes (N) required to completely cover the image, Log (N) and Log(r) computed, is recorded and stored in a file for further use.

(a) (b) (c)

Figure: 4: Showing electro-less deposition obtained with a 1 molar $CuSO_4$ solution
a) Original Image b) Process Image c) Monochrome Image

The counting course of action continues up to a box size becomes less than 1/3rd the Faret's diameter. A table recorded for the analysis of Fig.4a as show in Table–1.

Table–1: Showing the box size and number of boxes required

Log(r)	*Log(N)*	*r*	*N*
0	4.4484	1	28077
0.301	3.907	2	8072
0.4771	3.6009	3	3989
0.6021	3.396	4	2489
0.699	3.2297	5	1697
0.7782	3.0993	6	1257
0.8451	2.9836	7	963
0.9031	2.8932	8	782
0.9542	2.8055	9	639
1.0414	2.6522	11	449
1.1139	2.5378	13	345
1.1761	2.4362	15	273
1.2304	2.3424	17	220
1.301	2.2405	20	174
1.3617	2.1038	23	127
1.415	2.017	26	104
1.4771	1.9191	30	83
1.5315	1.8513	34	71
1.5911	1.7324	39	54
1.6435	1.6628	44	46
1.699	1.5682	50	37
1.7559	1.4771	57	30
1.8062	1.415	64	26
1.8573	1.2788	72	19
1.9085	1.2553	81	18
1.959	1.1461	91	14

A graph is plotted with Log(N) on the y-axis v/s Log(r) on x-axis. This shows that almost all points fit to a straight line as shown in the Fig.5.

From the Fig.5 plot, it is observed that all the points of the plot follows the straight line for all the plots indicating that the dendritic patterns in electro-less deposition exhibit self-similarity over entire region of the length scale used as shown in Fig.4a and therefore confirms the fractal character of these dendritic patterns. From the plot, the fractal dimension of the given figure show that the all fractal dimension is about 1.67 indicates that crowded and dense branching with primary, secondary and tertiary branches and resembles to DLA characteristics [9-14].

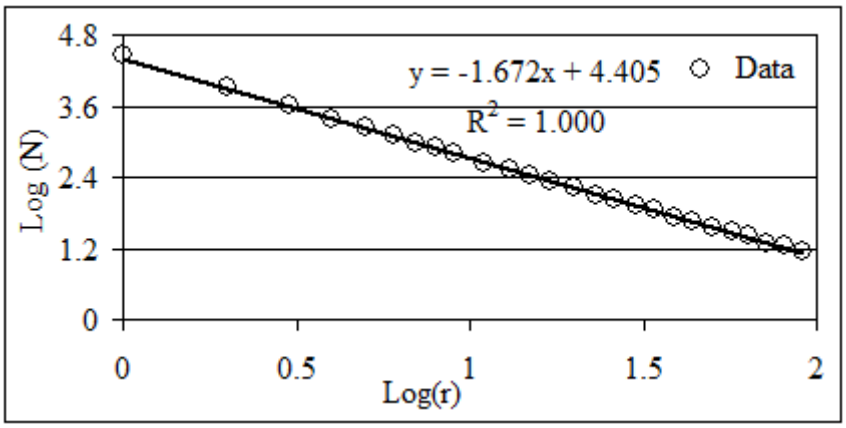

Fig.5: Log(N) versus Log(r) Plot for results of box counting of Fig.4c

IV. CONCLUSIONS

Electro-less deposition cell was constructed using glass and aluminum plates to study electro-less deposition of copper dendritic growth pattern of 1 molar copper sulphate solution. It is observed that after setting up the cell, the nucleation start after 1-2 hours in the form of fine spot, then some of the spots grow in pattern, others into lumps and very few of them in to beautiful dendritic pattern obtained which shows the fractal nature and self-similarity. Some of the growth is rapid while others are relatively slow. Electro-less deposition took around 8-10 hours for full-grown pattern.

It is also observed that growth is more common near to the edge compare to the rest of the portion. It is seen that if the spacing between the plates kept constant the fine branch pattern obtained. The physical strength of the branches is not too strong; it starts dislodging from the substrate as time progress and it also start to change in color from brownish to black. Number of factors affected the growth of dendritic pattern such as humidity, temperature, and air convection in addition to that type of paper with different thickness and concentration of the electrolyte solutions.

It is also observed that the fractal dimension of a growth depending on the complexity of structure and texture connected with the pattern and they are governed by DLA like processes.

Conflict of Interest: The authors declare that they have no conflict of interest.

Ethical Statement: The authors declare that they have followed ethical responsibilities.

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