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Effect of free energy barrier on pattern transition in 2D diffusion limited aggregation morphology of electrodeposited copper

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Abstract

Fractal like morphology is a very interesting feature during electrodeposition of metals and shows pattern transition with changes in deposition conditions. In this article, we have explained the thermal effects in the two dimensional DLA morphology on the basis of thermal free energy and another free energy barrier resulting from the electric field. The results obtained from free energy hypothesis are consistent with experiments showing the transition voltage for electrodeposition of copper ions to be around 6 V.

Keywords: Materials science, Electrochemistry

1. Introduction

It is well known [1] that ultra - thin copper films, prepared through electrochemical deposition are extensively used in the electronics industry e.g. to fabricate the printed circuit boards and electric lead in narrow bezel touchscreen owing to their high electrical conductivity. Systems like Ni-Cu and Co-Cu involving

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copper have also been studied extensively [2, 3]. During electrochemical deposition of the copper films, fractal-like patterns have been observed by many authors [4, 5]. Thus, the growth of such ultrathin 2D like copper film is a very interesting field in understanding the underlying ion dynamics. It has been extensively studied both experimentally and theoretically [6, 7] with the help of models like Diffusion Limited Aggregation (DLA) [8] which is the process whereby particles undergoing a random walk due to Brownian motion cluster together to form aggregates of such particles and Dielectric Breakdown Model (DBM) [9] which combines DLA with electric field. These studies have mostly focused on the growth phenomena and morphological transitions [10, 11, 12]. Though DLA and DBM explain the growth phenomena, but the microscopic theory used in both to explain the physical mechanism of the morphological transitions is not completely understood due to the complex multi-parametric dependencies on the growth phenomenon. Therefore, the theoretical and experimental works have been largely confined to finding those parametric dependencies [13]. It has been hypothesized [5] that if the problem of morphological transition during electrodeposition is seen in momentum space with ionic velocity driven by thermal and electric fields, the experimental results can then be explained satisfactorily. Though great qualitative insight has been gained from these studies, but still many questions on how the morphological transitions change with temperature remains less explored.

It was reported [5] that fractal dimension for fractal like growth during copper electrodeposition decreases with increasing electric field and molarity, but interestingly it follows an inverse relation below 6 V. We perform similar experiment again and found the transition voltage to be 6 V. In this article, we report on how temperature affects the deposition process and then the microscopic physical mechanism will be discussed in order to explain the morphological transition.

2. Experimental

The experimental setup was designed using thin square glass slabs of side 6 cm with thin copper strips as electrodes so as to ensure two dimensional growths during electrodeposition process. The electrolyte used was 0.05 M copper sulphate solution. At first, the gap between the electrodes was kept to be 3 cm and the voltage was varied at room temperature conditions (35 °C). The pattern changes were observed and images were taken using DSLR Camera. Next the temperature of the solution was varied by keeping the voltage fixed at 10 V. The temperature was kept fixed by using constant temperature bath inside a closed thermal system where the electrodeposition process was carried out. The pattern changes were again observed and images (Fig. 1) were taken using DSLR Camera.

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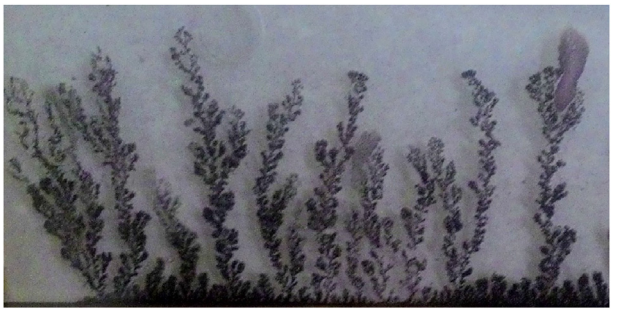

Fig. 1. The fractal like growth for copper electro-deposition obtained at negative electrode for temperature 35 °C.

3. Results and discussion

Each image obtained by variation of temperature was analyzed and the fractal dimension was obtained using box counting method where, each image was covered by a grid and the no. of boxes covering the image was counted (N). The fractal dimension was then given by Eq. (1)

$$F_d = (log\ N)/(log\ r) \quad (1)$$

where r is the magnification or inverse of box size. Fig. 1 shows the image of fractal like deposition for illustration purpose.

Fig. 2 shows the variation of fractal dimension with temperature in the experiment. According to the graph the fractal dimension increases with rise in temperature.

When an atom or a molecule or an ion hits a solid surface, it can only stick at the surface if it loses its kinetic energy. As the temperature rises, the ions have a greater probability to escape the attraction of negative electrode, but due to successive collisions, they lose their kinetic energy and with time, fall into the potential well. Hence a higher temperature causes a low sticking probability for the ions.

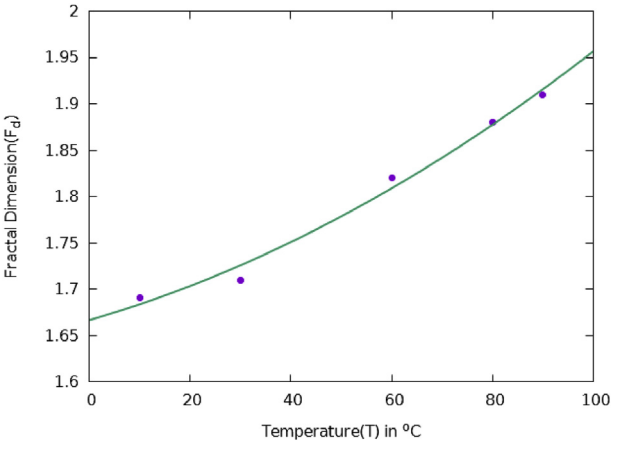

Fig. 2. Variation of fractal dimension with temperature keeping voltage fixed at 10V.

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In order to find the detailed relation between the sticking probability and temperature, simulation of dissociative sticking of copper ions in thin gap geometry was done following the DLA algorithm [8]. A rectangular lattice was used for simulation purpose and not a triangular lattice as if it were chosen, the branches would go towards the corner which is unlikely to be observed in case of copper fractals [14]. The number of particles was kept constant. Using standard DLA simulation, the graph of the parametric variation of the sticking probability in terms of fractal dimension is obtained as shown in Fig. 3.

With the experimental data and simulation, a relation between sticking probability and temperature is found to be as given in Eq. (2),

$$S = S_0 \, exp \, (-E_a/k_B T) \tag{2}$$

where, E_a the activation energy is and k_B is the Boltzmann constant. This relation is very similar to absorption cases [13] and suggests a thermodynamic activation barrier for the deposition due to the temperature dependence of the sticking probability. In order to understand the behavior of the thermodynamical barrier, it is very important to calculate the free energy of the system.

For the free energy calculation in thin gap geometry (6 cm $\times$ 3 cm), a two dimensional lattice with size (600 $\times$ 300 pixels) was used. At first, the Di-electric Breakdown Model was used to simulate the electrodeposition process. Then the distribution of electric field was calculated over the lattice using laplace method. In the simulation, it is assumed that H^+ ions and SO_4^{2-} ions are not affecting the whole deposition dynamics and only rotational energy is associated with the Cu^{2+} ions. Both the thermal and electric free energy were calculated separately for proper experimental insight. In order to calculate the free energy in aqueous medium, we considered the partition function given by Eq. (3)

$$Z = exp \, [\{m(v_{th}^{\,2} + v_d^{\,2})\}/2k_B T] \tag{3}$$

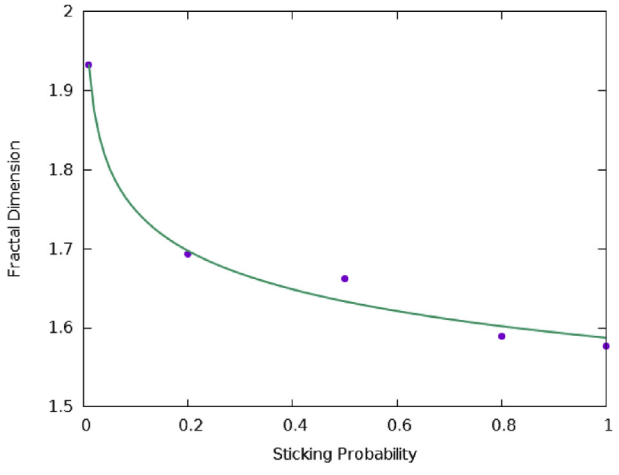

Fig. 3. Variation of fractal dimension with sticking probability.

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where, v_{th} is the thermal velocity and v_d is the drift velocity caused by the medium and the applied voltage difference, m is the mass of the ion and k_B is the Boltzmann constant. From the simulation, we get the variation of free energy, F_{Th}, with temperature as shown in Fig. 4.

Now if we consider the situation without the aqueous medium, the partition function becomes (Eq. (4))

$$Z = exp\ [(mv_{th}{}^2 + \varepsilon_0 E^2)\}/2k_B T] \tag{4}$$

where E is the applied electric field and T is the temperature kept fixed at 35 °C. The variation of the free energy, F_E, with electric field is shown in the inset graph of Fig. 4. An interesting correlation can be drawn from these two plots. Below 7 V, the electric free energy barrier is lower but the thermal barrier is higher. When the thermal effect leads, the growth area becomes proportional to the number of particles in solution. Moreover, few ions reach the negative electrode due to high thermal free energy barrier causing less area of growth at lower voltages. Now, as the electric field is increased, thermal effects reduce. The electric free energy barrier increases and consequently fewer ions can overcome resulting in less area of growth. As the growth area first increases and then again starts decreasing, there is a morphological transition which occurs. From Fig. 4, it is seen that free energy value is −0.312 eV at 35 °C. From the inset graph, it can also be noted that the value of electric free energy is 0.312 eV for 6 V at 35 °C. Hence 6 V is the barrier electric field needed to overcome thermal energy value. Thus, it is due to overcoming of this electric field that morphological transitions take place and a reversal in pattern is shown which is consistent with the experiment.

Further, the discontinuity of the first derivative of the quantity $|F_E - F_{Th}|$ is calculated and plotted as a function of electric field shown in Fig. 5. This graph suggests in favor of the above important parameter to understand the path of transition voltage with various other parameters.

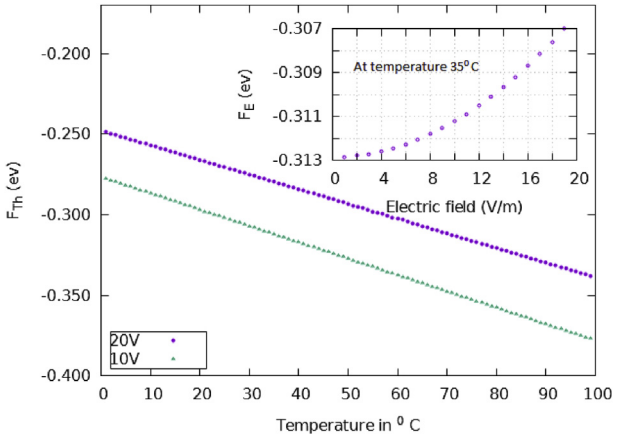

Fig. 4. Variation of thermal free energy (F_{TH}) barrier with temperature at different constant electric field [Inset: the variation of surface electric free energy (F_E) of the molecules at 35 °C using statistical ensemble theory].

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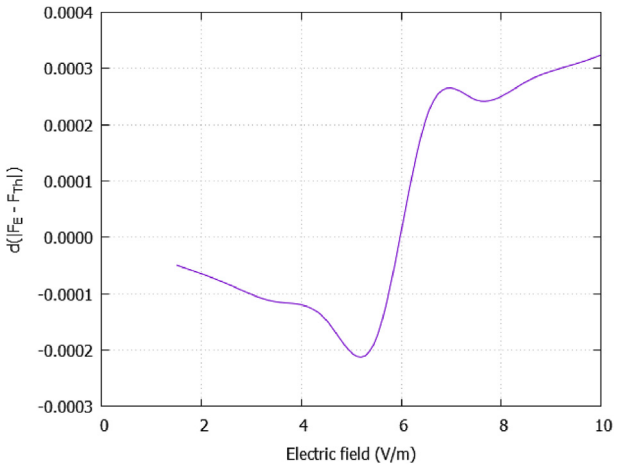

Fig. 5. First derivative of the quantity $|F_E - F_{Th}|$.

4. Conclusion

In summary, it was found that morphological changes in electrodeposition under thin gap geometry are governed by free energy barriers. Higher electric free energy barrier causes fractal like deposition and higher thermal free energy causes clustered deposition. The results obtained from free energy hypothesis are consistent with experiments which gave the transition voltage for electrodeposition of copper ions to be around 6V.

Declarations

Author contribution statement

Souradeep Ghosh, Raveena Gupta, Subhankar Ghosh: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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