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Influences of magnetic field on the fractal morphology in copper electrodeposition

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Abstract. Copper magneto-electrodeposition (MED) is used decrease roughening in the copper electrodeposition process. This technology plays a vital role in electrodeposition process to synthesize metal alloy, thin film, multilayer, nanowires, multilayer nanowires, dot array and nano contacts. The effects of magnetic fields on copper electrodeposition are investigated in terms of variations in the magnetic field strength and the electrolyte concentration. Based on the experimental results, the mere presence of magnetic field would result in a compact deposit. As the magnetic field strength is increased, the deposit grows denser. The increment in concentration also leads to the increase the deposited size. The SEM image analysis showed that the magnetic field has a significant effect on the surface morphology of electrodeposits.

1. Introduction
Electrodeposition plays a very important role in various types of industries. Electrodeposition is not only used to enhance the face value of metal articles by improving the appearance aesthetically but electrodeposition is also used to improve contact resistance, reflection properties of materials and to impart friction properties [1]. The problem of obtaining a uniform, dense and compact deposition is the problem in electrodeposition. There are numerous studies that had been carried out to reduce it [3. 7 8]. One of the methods of tackling this problem is MED. It had been found that different strength of magnetic field will affect the growth pattern and its morphology [7, 8]. Moreover, in the MED technology, the electrolyte concentration is also a crucial factor in determining the growth pattern of the deposited metal [9]. The objectives of this work are to study the effect of magnetic strength on growth fractal and its morphology of copper electrodeposits. The influence of electrolyte concentration towards growth fractal also has been studied.

2. Experiment Procedure
The copper fractal electrodeposits were developed in a flat circular cell with a copper wire cathode (1 mm in diameter) at the center and a copper ring anode (thickness 0.5 mm, outer diameter 70 mm and inner diameter 50 mm) as shown in Figure 1. The distance between anode and cathode was 49.5 mm. Copper sulfate solutions of various concentrations were made up using $CuSO_4 \cdot 5H_2O$ in distilled water. The $CuSO_4 \cdot 5H_2O$ concentration was varied in the range from 0.1 to 0.75 M in 0.5 M H_2SO_4. The depth of the aqueous film can be varied by regulating the total volume of the $CuSO_4$ solution. The copper was electrodeposited with a voltage of 6 V. A Ferrite and Neodymium permanent magnets

were used to provide a weak (300 gauss) and strong (900 gauss) magnetic field, respectively. The resulting fractal patterns were photographed using a digital camera and then analyzed using Matlab image processing. A mass microbalance was used to measure the mass of fractal electrodeposits. The maximum diameter of fractals was measured using a ruler. The surface morphology of fractal electrodeposits was analyzed and characterized using scanning electron microscopy (SEM).

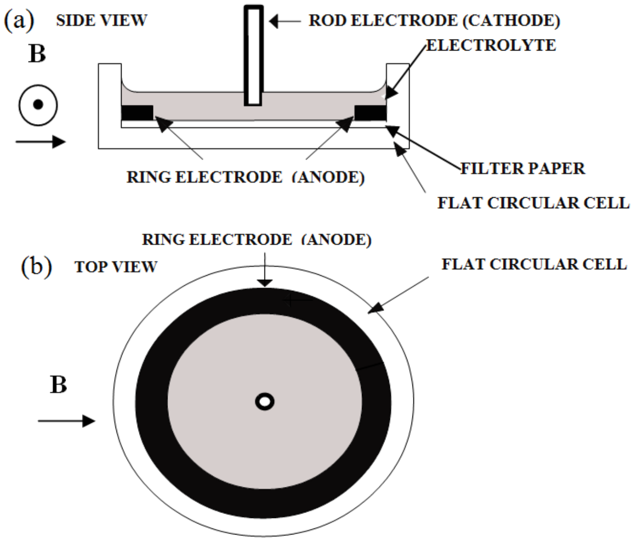

Figure 1. Schematic diagram of a flat circular electrochemical cell to investigate the growth fractal produced via MED: (a) side view (b) top view

3. Result and discussion

3.1. Effect of Electrolyte Concentration on Magnetic Electrodeposition

From figure 2a to figure 2e, we found that the dendritic structure grows larger and more compact as the concentration of $CuSO_4$ increases. As the concentration increases, the tiny dendritic structure in Figure 2a branched out further to a state as shown in figure 2e. Then, the dendritic structure becomes denser when the concentration was increased to 0.2 M. At 0.5 M, the dendritic structure already achieved a dense branching morphology (DBM) state [12]. Since the concentration keeps increasing, the dense branching morphology will inhibit more copper from depositing within it. Thus it will cause the aggregate structure to spread out. Consequently, as the concentration used is increased to 0.75 M, the electrodeposited copper had DBM as well as protruding dense branches from the DBM structure as shown in figure2e.

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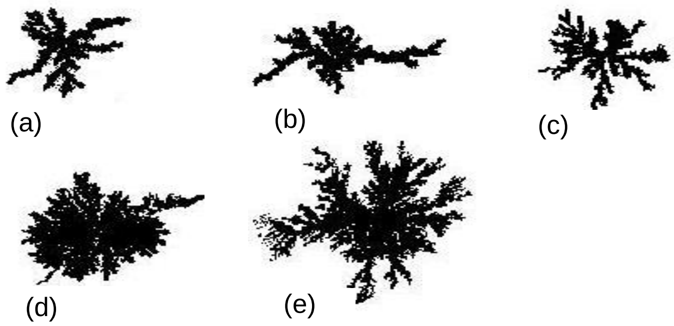


Figure 2. Copper electrodeposits (applied voltage of 6 V, neodymium magnet, time duration 20 minutes) : (a) $CuSO_4$ 0.1 M, (b) $CuSO_4$ 0.15 M, (c) $CuSO_4$ 0.2 M (d) $CuSO_4$ 0.5 M (e) $CuSO_4$ 0.75 M

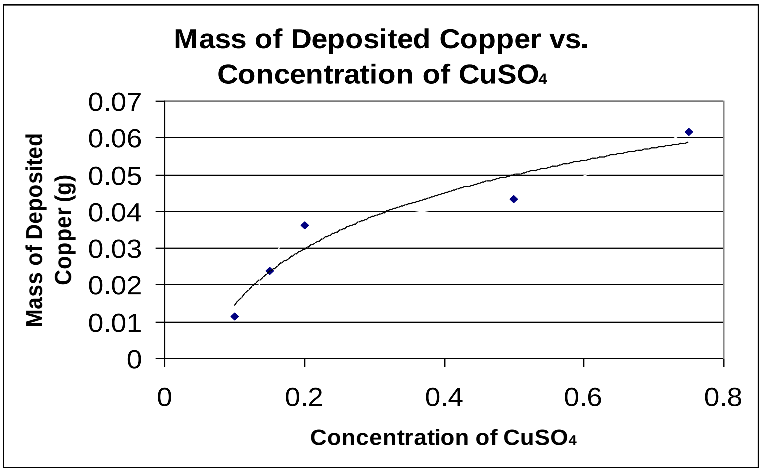


Figure 3. Mass copper electrodeposits in variation concentration of $CuSO_4$

Besides that, when the concentration is increased, the mass of the deposited copper will also increase accordingly as seen in Figure 3. This increment of growth pattern and the mass deposited can be linked to the increasing concentration of the $CuSO_4$ in the electrolyte. As the concentration increases, so do the free cations (Cu^{2+}) available in the electrolyte. These free cations are more ready to be deposited at the deposition area to form the deposited metal [14]. As the quantities of these free cations increases so do the deposition intensity per unit area. This will result in a higher rate of copper deposition as well as produce an aggregate with higher mass and larger in size.

The increment in concentration also will increase the collision rate of the species within the electrode. It is due to the increasing quantity of substances within a unit area. As the collision rate increases, it will also induce a turbulent flow of the electrolyte. In return, this will increase the flux of the species [13]. As a result, the thickness of the Nernst diffusion layer will gradually be reduced and this will decrease the screening effect too. The magneto-hydrodynamic (MHD) effect caused by the magnetic field will also decrease the screening effect at the deposition site [2, 12]. When the screening effect of the Nernst diffusion layer decreases, more same charged cations are able to converge at any single point at the deposition area without being repulsed away [15, 16, 17]. Thus, more cations are able to discharge at the deposition site which will results in a denser, larger and heavier growth as shown from figure. 2a to figure 2e and figure 3.

However, based on figure 3, when the concentration of the $CuSO_4$ in the electrolyte is increased, the mass of the deposited copper increases not in a linear fashion. The increment tends to be greater when the concentration range is lower and decreases as the concentration increases. This observation occurs as a further increment of concentration will result in the increase of cations. The high amount of cation will increase the cathodic polarization and decreases the anodic polarization. The polarization occurred will reduce the difference in potential between anode and cathode to a minimum [1]. Consequently, it tends to resist the flow of the current to the cathode. Thus, the increment in the mass of deposited copper is reduced. Similar observations are made when the experiment is conducted with variation in the electrical potential supplied.

3.2. Effect of Magnetic Field on Surface Morphology

When conventional electrodeposition is carried out without the magnetic field influence, it is observed that the copper fractal formed a diffusion limited aggregation (DLA)-like structure (figure 4a). The fractal pattern becomes denser and compact as the increase of magnetic field as shown in figure 4b. This phenomenon is due to the presence of MHD effect (figure4b). This MHD effect is actually generated by the magnetic force and as the magnetic field strength increases, the strength of the MHD effect increases as well. This MHD effect acts by reducing the thickness of the Nernst diffusion layer. When the thickness is reduced, the screening effect within the layer is reduced as well [2, 12]. Then, more copper ions are able to release at a given point in the deposition area. Hence, the overall aggregate will become more compact. Consequently, the mass deposited will also increase.

The MHD effect also will cause a turbulent flow near the deposition area which will enhance the ionic mass transfer. The additional metal ion introduced by the turbulent flow will also encourage more side branches to develop beside the main branch.

(a) (b)

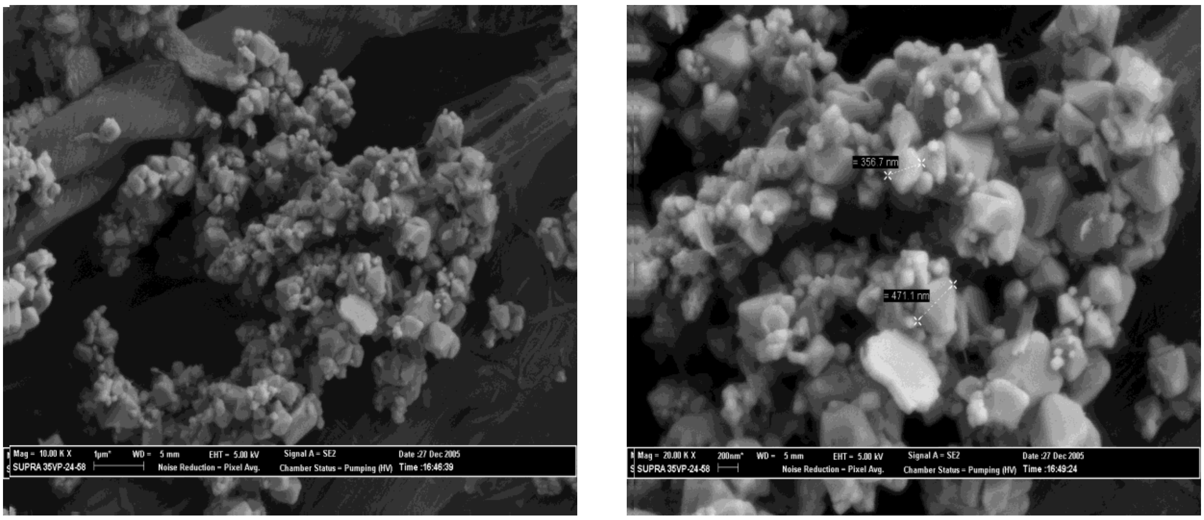
Figure 4. Copper electrodeposits (applied voltage 6 V, $CuSO_4$ 0.2 M, time duration 20 minutes): (a) without magnet, (b) in strong magnetic field [18]

Figure 5a shows the SEM image of copper electrodeposited with the absence of a magnetic field. The long cylindrical structures in the diagram are the fiber strands of the filter paper. Each of the tiny clusters represents a new nucleation point and when aggregated together, it forms the domain of the electrodeposited copper as in the figure 5a. Even at a microscopic level, the overall domain of the deposited copper is sparse. Each of the domains is situated far away from each other and it also seems to be coarse. At a higher magnification (figure 5b), the tiny cluster of deposited copper within the domain is found to be highly inconsistent in its size and shape. Some clusters are big and some are small. The shapes of the cluster are also highly irregular. Even as the surface of a tiny cluster may seem to be smooth; however, when aggregated together, the overall domain surfaces are found to be coarse.

Figure 6a shows the SEM picture of the copper deposited in the presence of an external applied magnetic field. It can be seen that the overall electrodeposited copper is much compact and uniform in shape. Most of the aggregate is also spherical shaped and it contains several large domains of 1-3.5μm in size. At a higher magnification (figure 6b), these domains are actually made up of tiny clusters of copper nanoparticles. These tiny clusters of copper nanoparticles indicate that fresh nucleation occurs and the growths of the particles take place uniformly under the influence of the magnet. The overall surface morphology of the domains and the clusters are also observed to be much smoother and uniform. Thus, the process of electrodeposition in the presence of an externally applied magnetic field is found to be assisting and increasing the fresh nucleation as well as the growth process. The cluster structure also tends to aggregate together and the surface is much smoother and regular. This observation can be explained via the magneto-hydrodynamic effect generated by the magnetic field.

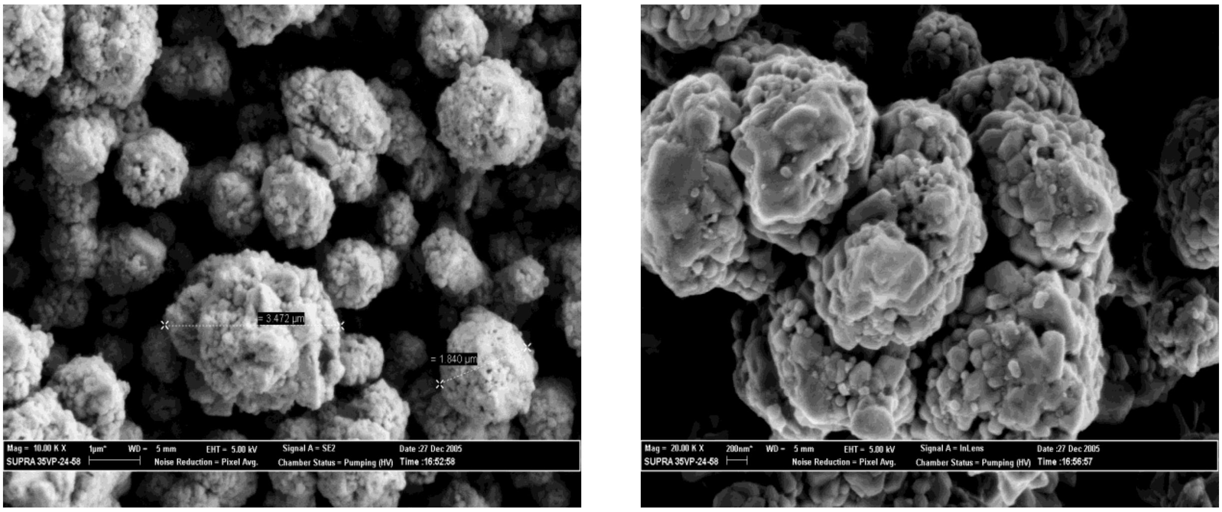
The MHD effect will increase the ionic mass transfer near the cathode surface by creating a convection flow near the electrodeposition area. Thus, the metal grains tend to grow uniformly and have a smooth surface in a magnetic field since the convection provide sufficient metal ions to each grain during the growing process.

The MHD convection also reduces the thickness of Nernst diffusion layer and the screening effect within it. As the screening effect is reduced, more metal ions are able to approach the electrodeposition side unhindered [15, 16, 17]. Fresher nucleation will occur and the growth of the new nucleation point also will be more uniform and fast as the result of the increasing quantity of copper ions.



(a) (b)

Figure 5. SEM photograph of copper deposited : (a) without magnet at 10.00 K X, (b) without magnet at 20.00 KX (higher magnification)



(a) (b)

Figure 6. SEM photograph of copper deposited: (a) under strong magnetic field effect (900 gauss) at 10.00 K X, (b) under strong magnetic field effect (900 gauss) at 20.00 KX (higher magnification).

4. Conclusions

Based on the result and discussion above, the increment of bath concentration as well as the magnetic field may result in a heavier deposit but one must bear in mind that the deposit may be large in size. Meanwhile, the increasing of the magnetic field will increase more compact and dense electrodeposits. The surface morphology of copper electrodeposits also shows that electrodeposits under magnetic effect more compact and uniform and shape. Hence, we can conclude that the introduction of magnetic field on electrodeposition able to improve the surface morphology of electrodeposits.

Acknowledgment

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