Simulation of the formation mechanism of a viscous layer for the electropolishing process

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Abstract

Electropolishing (EP) is a surface finishing treatment method. The surface quality indices such as surface roughness, cleanness and corrosion resistance could be improved through this process. Because of these benefits, the electropolishing process is applied to fabricate high cleanness apparatus for semiconductor and optical pharmaceutical industries.

Electropolishing is an electrochemical reaction process. The uniform and stable passive film is the key mechanism in enhancing the surface quality. However, the forming of passive film is influenced by the current distribution, fluid field and diffusion phenomena. Therefore, there are many defects such as pits, flow marks and scrape which could be found after the electropolishing process. These defects destroy the uniformity of the surface quality and induce local corrosion.

The goal of this study is aimed at simulating the formation of a viscous layer and establishing numerical a model to predict its thickness and uniformity. In this study, the commercial software of FEMLAB was employed to establish a multi-physics model which contained the effects of fluidity and diffusion. The mechanism of passive film formation, the influence of fluid velocity and the thickness variation of the viscous layer were investigated through numerical simulation.

Keywords: electropolishing, passive film, numerical simulation, multi-physics.

1 Introduction

The electropolishing is a precision surface finishing treatment method. It could enhance the cleanliness and smoothness of a specimen. The thin passive film formed on the surface will also improve its corrosion resistance [1-3]. The process is composed of an anode (specimen), a cathode and acidic electrolyte. During the process, hydrogen will be generated on the cathode while oxygen on the anode. The metallic ions react with the electrolyte to form diffusion layer, also called viscous layer, on the surface. This diffusion layer is the key factor that controls the leveling, polishing and passivity mechanisms of the electropolishing process.

Many researchers define the diffusion process as the controlling mechanism of the EP process [4-6]. However, there are other effects such as convection, temperature distribution, gas bubbles and electron migration taking place at the same time which makes the whole process multi-physics phenomena. Hence, the control of the initiation and stability of the diffusion process becomes very complicated. Eventually, they affect process parameters of electrode gap, polishing time, applied potential and electrode design.

Therefore, the diffusion layer formed under diffusion control is fragile and unstable. It may be easily affected by the process and has become the key factor in achieving process control and product quality. The method of rotating disc electrode (RDE) was proposed and was reported to have beneficial effects on the EP process [7-8]. Mechanical agitation of the electrolyte seemed to also have the same effects [9-10]. Many research results pointed out refreshing of the electrolyte by fluid control can improve EP polishing effects and process stability.

However, due to the lack of understanding on the formation mechanism of the diffusion layer, various researches chose vastly different process parameters for their experiments [11-13]. In order to gain deeper insight, this paper employed FEMLAB, a commercial code, to simulate the effects of diffusion and convection on the diffusion layer.

2 The problem statement

During the EP process, the ionic concentration on the electrode surface is varying. For example, the metallic ions will dissolve from the anode and react with electrolyte. This will increase the concentration of metallic ions on anode surface. The concentration gradient results in the formation of diffusion layer which, in turn, creates the plateau region of the I-V curve.

In this research, numerical simulations were performed to study the effects of the electrolyte flow to the diffusion layer. The schematic plot of the electropolishing process was shown in Figure 1(a). Assumptions of incompressible fluid, laminar flow and constant temperature were made in order to simplify the numerical model.

In the electrochemical reactions, the transport phenomenon was composed of the ionic migration, diffusion, convection and electron flow. If the concentration of electroactive species is low, the interaction between molecules could be ignored. Hence, the mass transfer in the electrolyte occurs under several physical phenomena; ionic migration under the influence of electric field, diffusion due to concentration grading, and convection. It is shown as follows:

$$Ni = -z_i u_i F C_i \nabla \phi - D_i \nabla C_i + C_i v \tag{1}$$

On the right hand side, they represent the effects of migration, diffusion and convection. Where z_i, u_i are the number of carrying electron and its coefficient of mobility for specie i, $\nabla \phi$ is the grading of electric field, C is the concentration and F is the Faraday's constant.

During the formation of diffusion layer, the polarization phenomena also take place simultaneously which will decrease the effect of migration. However, the fluid dynamics has much greater effects on the formation of diffusion layer and its stability. Therefore, the effects of electron migration were ignored in this study. The effect of gas bubbles makes the fluid dynamics a two-phase flow problem which increases the complexity on numerical simulation considerably. Therefore, it was also ignored. The numerical model had been simplified to the study of diffusion and convection under various fluid field velocities.

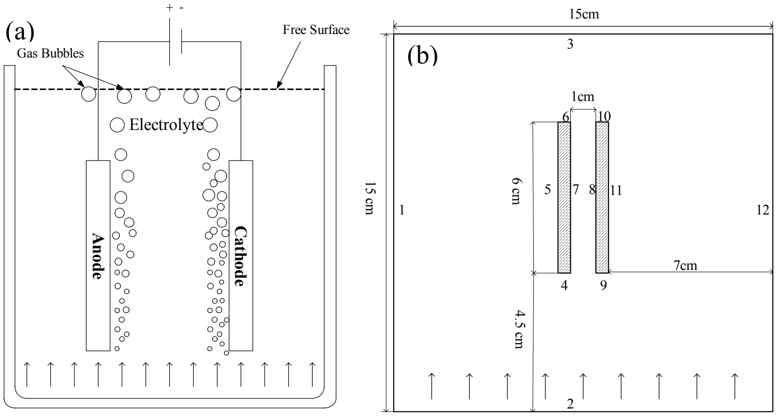

Figure 1: (a) Schematic picture of the EP process. (b) The specifications of the model.

2.1 The model specification

This study mainly concerns the phenomena of diffusion layer in between the electrode gap. Therefore, problem definition was focused around the electrode area. The geometry and specification of the 2D model was presented in Figure 1(b). The model specifications remained the same throughout this study. The entire flow fluid area is 15 cm by 15 cm. The area of both anode and cathode was 0.6 cm^2. A jet flow pattern from the bottom of the tank, boundary no. 2, with uniform speed was assumed. The boundaries were assigned with numerical number, as showed in Figure 1(b), for boundary specifications.

2.2 The diffusion and convection model

The Fick's law is the governing equation in diffusion and convection model, shown in Equation 2. Since steady state is assumed, hence, the rate for chemical reaction is 0, shown in Equation 3.

$$\frac{\partial C}{\partial t} + \nabla(-D\nabla C + Cu) = R \tag{2}$$

$$\frac{\partial C}{\partial t} + \nabla(-D\nabla C + Cu) = 0 \tag{3}$$

where C: concentration of diffusive species, D: diffusion coefficient, u: velocity of fluid, R: rate of chemical reaction.

The diffusion mechanism of the EP process is defined as ordinary diffusion liquid. Because it is very hard to measure the diffusion coefficient, the diffusion coefficient was estimated from the Storkes-Einstein equation, as presented in Equation 4. Although the precision of the Storkes-Einstein equation is not good, it is our best available tool.

$$D = \frac{\kappa T}{6\pi\mu R} \tag{4}$$

where D: diffusion coefficient, κ :Boltzmann's constant, μ :Viscosity of electrolyte, R: Solute radius.

2.3 The fluid field model

Because turbulence will affect the uniformity of the reaction rate and result in lack of process control, it should be avoided in the flow of electrolyte. Therefore, the conventional Navier-Stokes Equation is adopted as the governing equation for the fluid field model. Equation 5 represents laminar fluid field in the tank of electrolyte.

$$\begin{aligned} &\rho\frac{\partial u}{\partial t} - \eta\nabla^2 u + \rho(u\cdot\nabla)u + \nabla p = F \\ &\nabla\cdot u = 0 \end{aligned} \tag{5}$$

where ρ : density, η : dynamic viscosity, u: velocity field, p: pressure, F: volume force.

2.4 The boundary conditions

In the laminar flow model, no slip condition, $u = 0$, is assumed for all boundaries except the inlet and outlet. The inlet, boundary no. 2, is assigned as inflow with constant flow speed in Y direction. In the diffusion and convection model, the reactant formed on the anode will diffuse toward the cathode. Hence, the concentration on the anode surface, boundary no. 7, was assumed to be one while it is zero at the cathode, boundary no. 8. The other boundaries, boundaries no. 1, 2 and 4-12, were not involved in the electrochemical reaction. Their flux values were assigned to be zero, $-D\nabla c + cu = 0$. Because the effect of convection is much stronger than diffusion at the outlet, boundary no. 3, there are outflow of flux from the outlet. Therefore, it is defined as convective flow, $-D\nabla c = 0$. The settings of boundary conditions were listed in Table 1.

Table 1: The settings of Boundary conditions.

Boundary settings of the flow model			
Boundary no.	1,4-12	2	3
Description	No slip	Inflow	Outflow
Setting	u=0	$u=(u_0,v_0)$	P=0
Boundary settings of the diffusion and convection model			
Boundary no.	1,2,4-12	3	7
Description	Flux	Convective flux	concentration
Setting	Flux=0		1

2.5 Computational parameters

Three levels of diffusion coefficient were selected to study the effects of its interaction with fluid field on the thickness and shape of the diffusion layer. They were 10^{-7}, 10^{-8} and 10^{-9}cm/s, respectively. In order to ensure laminar flow, the velocity of fluid should be slow. The initial speeds at the inlet were assigned as 1cm/s, 0.5cm/s and 0.1cm/s. In order to have the same bases for comparison, the simulation duration was set at 300 seconds for all analyses.

3 Results and discussions

First, the numerical simulations with no fluid field were performed to be taken as the references. Three levels of diffusion coefficient were considered in the simulation. When the level of concentration is higher than 90%, it was considered as the viscous layer. Because the viscous layer is the most important mechanism in controlling the EP process, the variations in the thickness and shape of the viscous layer were the focus in this study. Figures 3, 4 and 5 represented the growth of diffusion layer over time for diffusion coefficients 10^{-7}, 10^{-8} and 10^{-9}cm/s, respectively.

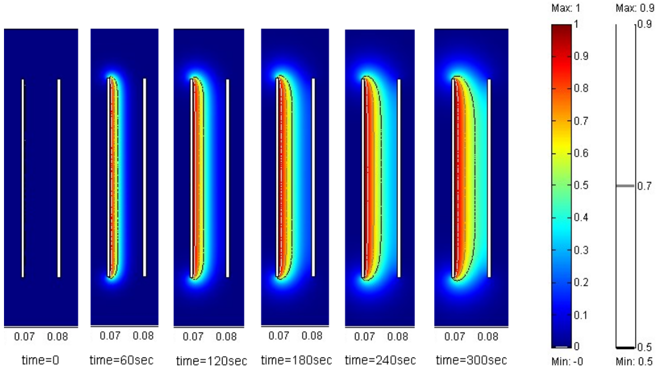

Figure 2: Profile of the diffusion layer, $D=10^{-7}$cm/s.

In Figure 2 where the value of diffusion coefficient was 10^{-7}cm/s, the diffusion process is still in transient state after 300 seconds. A steady state is not reached. The diffusion layer is still changing with time. The results may reflect the fact that the impendence variation between the electrode gaps is too large for the EP process. Therefore, the process is hard to control and the uniformity may not be good.

When the diffusion coefficient is 10^{-8}cm/s, shown in Figure 3, the diffusion speed is slower. It reached steady state in 180 seconds. It may indicate that the impedance in between the electrode gap is more stable. The thickness of the diffusion layer is thin and dense. For the leveling mechanism of the EP process, a thin and dense diffusion layer provides better selective dissolution and, thus, better polishing results and uniformity.

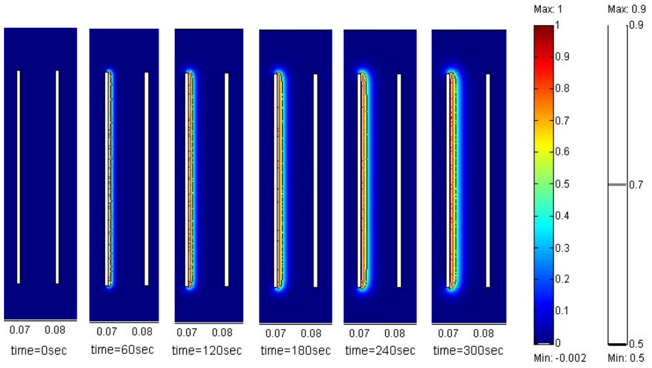

Figure 3: Profile of the diffusion layer, D=10^{-8}cm/s.

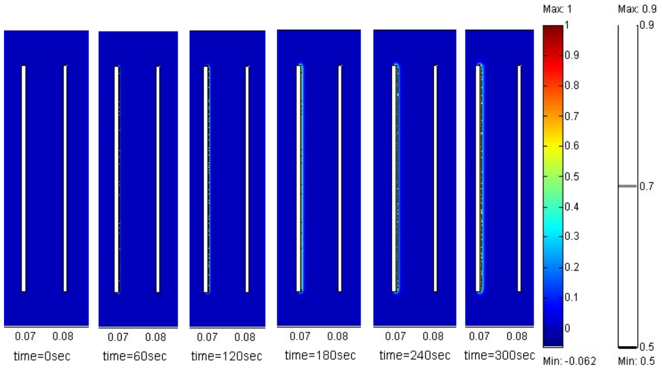

Figure 4: Profile of the diffusion layer, D=10^{-9}cm/s.

When the diffusion coefficient is as low as 10^{-9}cm/s, it is very hard to diffuse, as demonstrated in Figure 4. It also reached steady state in 180 seconds. However, the thickness of the diffusion layer was only a few tens of micrometers. Ideally, it may result in very smooth surface. However, it is very hard to maintain a uniform diffusion layer of such thin thickness. Therefore, it is estimated that the diffusion coefficient of the EP process should be between 10^{-7}cm/s and 10^{-8}cm/s.

The following simulation analyses of fluid field on the EP process will be performed on these two values of diffusion coefficient.

3.1 Results of fluid field simulation with diffusion coefficient D=10^{-7}cm/s

Figure 5 showed the simulation results of flow speed equals to 1 cm/s. The diffusion layer was stabled down after 60 seconds. Comparing Figure 5 to Figure 2, the stability of the impedance in between the electrode gap had shown significant improvement. However, there were greater variation at both the inlet and the outlet due to stronger fluid dynamics effect. From the contour line of 90% concentration level of Figure 5, it was found that the thickness of the viscous layer had grown from 0.05mm at the inlet to 0.1 mm at 1mm distance along the Y-axis toward the outlet. It had grown further to 0.2mm at Y=3.8mm, to 0.3mm at Y=13.2mm, to 0.5mm at Y=17mm and finally to 2mm at the outlet. The difference in the thickness of the viscous layer was ten folds. It will result in differences in the metallic dissolution rate at both the inlet and the outlet and, thus, the lack of uniformity of the overall EP polishing results.

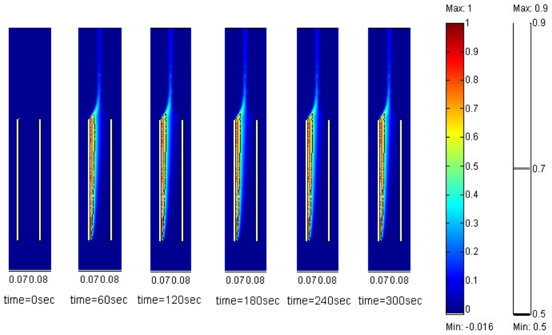

Figure 5: Profile of the diffusion layer, D=10^{-7}cm/s, V=1cm/s.

Figure 6 showed the simulation results of flow speed equals to 0.5cm/s. The diffusion layer had reached stable state after 120 seconds. However, it had the same problems of significant variation in the thickness of the viscous layer between the inlet and the outlet. The difference in between the thinnest and the thickest was also ten folds.

The diffusion layer had reached stable state after 180 seconds for the simulation results with flow speed equates to 0.1cm/s, as shown in Figure 7. The distribution of viscous layer was from 0.1mm to 0.9mm in thickness. The difference was only nine folds, the least in these three sets of simulation analyses. The thickness and shape of the viscous layer were better in comparison with Figures 6 and 7.

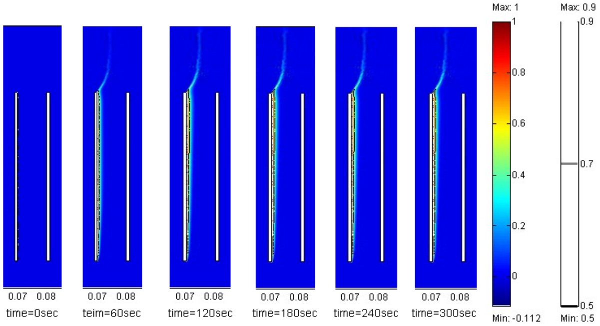

Figure 6: Profile of the diffusion layer, D=10^{-7}cm/s, V=0.5cm/s.

From the above simulation results, it could be concluded that, when the value of the diffusion coefficient is 10^{-7}cm/s, the fluid field could significantly reduce transient time. Shorter transient time meant less variation in the impedance in between electrode gap and, thus, better process uniformity. However, higher flow speed will result in significant differences in the thickness of the viscous layer. A ten folds difference was computed for the flow speed equals to 1cm/s. Therefore, slower flow speed was preferred.

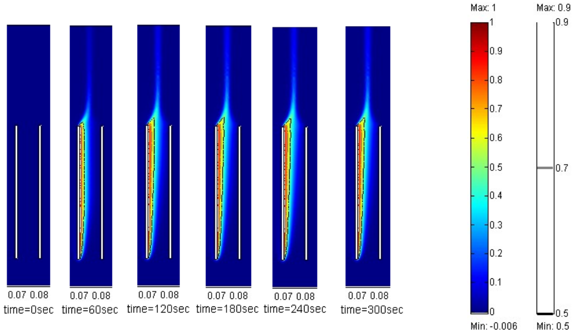

Figure 7: Profile of the diffusion layer, D=10^{-7}cm/s, V=0.1cm/s.

3.2 Result of fluid field simulation with diffusion coefficient D=10^{-8}cm/s

Figure 8 showed the simulation result of flow speed equals to 1cm/s. The results indicated that stability of the diffusion layer could be reached in 60 seconds, a significant reduction from 120 seconds with zero flow speed. The thickness of the viscous layer was 0.05 mm at the inlet and was 0.1 mm thick at Y=5.4 mm. It reached 0.2 mm thick at Y=42.4 mm and maintain stable afterward. The difference between the inlet and the outlet was only four folds. The uniformity was very much improved from the results with diffusion coefficient D=10^{-7}cm/s where the difference is ten folds.

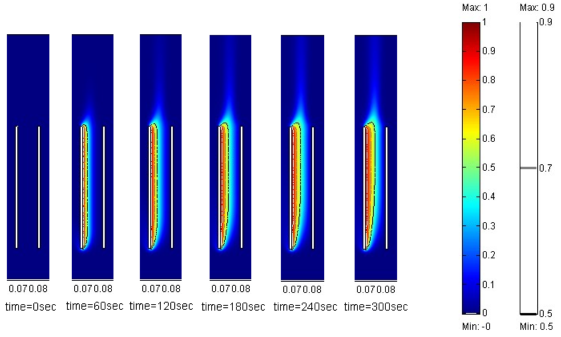

Figure 8: Profile of the diffusion layer, D=10^{-8}cm/s, V=1cm/s.

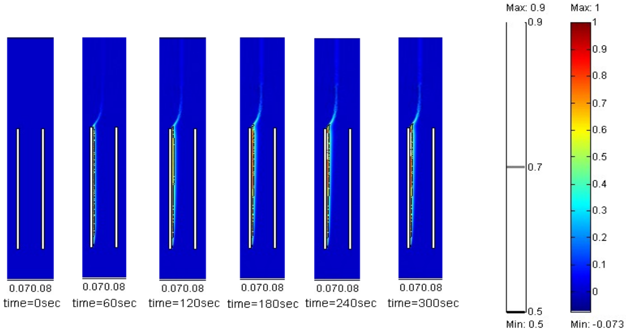

Figure 9: Profile of the diffusion layer, D=10^{-8}cm/s, V=0.5cm/s.

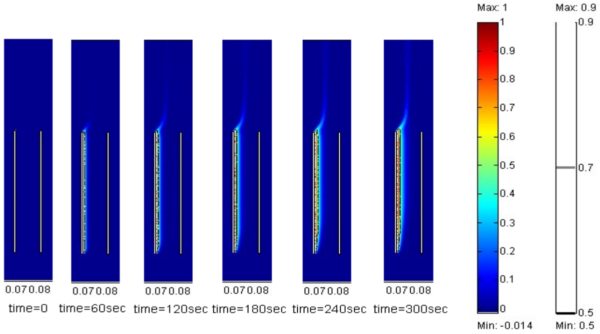

Figure 10: Profile of the diffusion layer, D=10^{-8}cm/s, V=0.1cm/s.

For flow speed equals to 0.5cm/s, the diffusion layer will reach stable state after 120 seconds, as shown in Figure 9. The distribution of the viscous layer thickness could be divided into four sections. From the 0.05 mm thick at the inlet, to 0.1mm at Y=4 mm, to 0.2 mm at Y=12 mm and maintain stable afterward. The shape and thickness of the viscous layer was even more uniform than in Figure 8.

For flow speed equals to 0.1 m/s, the diffusion layer will reach stable state after 180 seconds, as shown in Figure 10. The diffusion layer became thicker. The viscous layer reached 0.3 mm thickness after Y=2.2mm and maintain through the entire anode length. The difference in thickness between the inlet and the outlet was six folds. The shape and thickness distribution of the viscous layer was the best for all analyses results.

In summary, the results of diffusion coefficient, $D=10^{-8}$cm/s, can reached the stable state about the same time as those of diffusion coefficient $D=10^{-7}$cm/s. However, the thickness and its distribution of the viscous layer were much better. The uniformity and stability of the viscous layer improve with the decrease in flow speed. However, the thickness at the inlet was still about 0.05mm which may create minor problem in uniformity.

4 Conclusions

1. When there is no fluid field, the diffusion takes very long time which may affect the uniformity of the EP process.
2. The electrolyte should have high coefficient of viscosity in order to increase the diffusion coefficient of the solute. Higher diffusion coefficient improves uniformity of the viscous layer.
3. The fluid field has significant effects on the diffusion mechanism. Proper flow speed may effectively reduce time of transient state, improve uniformity of the viscous layer and enhance the overall polishing effects.
4. It is possible to increase process control and polishing precision by adjusting the fluid field to affect the distribution and the thickness of the diffusion layer.
5. Through the numerical simulation model, the diffusion mechanism of the EP process could be better understood. Process parameters could be analyzed to improve process control.

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