— Article —

Simulations on the Optimum Conditions for Propargyl Alcohol to Function as a Shape Control Agent in the Process of Nickel Electrodeposition onto a Micropatterned Substrate

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It was found that the addition of propargyl alcohol (PA) to a nickel sulfamate solution was effective for controlling the shape of deposit in the process of nickel electrodeposition onto a micropatterned substrate. The factors, *i.e.* the electrode potential, the thickness of diffusion layer and the concentration of PA, that affect the shape control function of PA were simulated by the boundary element method, based on the assumption that PA is consumed by diffusion-adsorption-reduction mechanism and that the concentration of PA vary along the cathode/solution interface. The function that represents the variation of PA concentration along the interface was used for the boundary values. The results of simulation explained well the difference in growing habit of the deposits obtained experimentally at different potentials, and figured out the important factors for suppressing the growth in horizontal direction. The optimum conditions for obtaining probe shape deposits were proposed.

Key Words : Electrodeposition, Additive, Shape Control, Simulation

1 Introduction

Electrodeposition of a metal or alloy onto a micropatterned surface has become an important technology in the electronics industry. The thin films so generated are used, for example, as conductors in multichip packaging modules or multilevel packaging structures, and as magnetic elements in thin film recording heads. In most cases, a pattern is generated in a layer of photoresist deposited over a thin conducting seed layer. The metal or alloy is electrodeposited onto those portions of the seed layer that are not covered by the resist. In these cases, the control of current distribution is important, for obtaining a desired shape of the deposit. The current distribution is controlled, in most cases, by the addition of a leveling agent. The functions of additives in leveling the electrodeposits have been reviewed by several authors.¹⁻³⁾ The current distribution of electrodeposition onto microprofiles in the presence of leveling agents was simulated by several authors.⁴⁻⁶⁾ In most cases, the current distribution was calculated under the conditions that the consumption of the additive is controlled by diffusion and the electrodeposition of the metal is far from diffusion limiting. In these studies, more strict considerations are desirable for the relation between the interfacial concentration of the leveling agent and its transport.

A method for growing a deposit beyond the level of the thin resist surface has been investigated by the authors⁷⁾ for the purpose of forming the probe shape deposit, which was formed usually by filling deep holes in thick photoresist pattern with the deposit. In that

study, a round shaped deposit was formed by using propargyl alcohol as an additive. This was the case that propargyl alcohol was used as a shape control agent. The several factors of propargyl alcohol, inhibition of nickel electrodeposition, diffusion, adsorption and reduction, have been studied from the polarization data using a rotating nickel disc cathode,⁸⁾ and the shape control function of propargyl alcohol in the process of nickel deposition onto a micropatterned substrate was proposed by the authors, comparing the simulation results with the experimental data.⁹⁾

In these studies, the diffusion-adsorption-reduction mechanism^{6,10,11)} is assumed for the consumption of the additive. The variation of additive concentration along the cathode/solution interface is especially important, because it strongly corresponds to the additive coverage of the cathode surface. In our simulation process, the function that represents the variation of interfacial concentration of propargyl alcohol was proposed and used for the boundary condition of the calculation, the simulated results of which explained the experimental results well.⁹⁾ It was reported by the authors that the organic compounds, which have C≡C bonding and OH group at the terminal carbon, have the shape control function equivalent to propargyl alcohol.¹²⁾ It was shown from the experiments and the calculations that the shape control function becomes less obvious as the deposit grows and the growth becomes isotropic on the deposits, the height of which are higher than about 15 μm.^{9,12)}

In this paper, we proceed with the study to step up

our previous simulation and try to figure out the important factors that affect the shape control function of propargyl alcohol. Two factors that represent to what extent the diffusion control the process and to what extent the reduction control the process are introduced, and the effects of these factors on the shape control function of propargyl alcohol are discussed. Finally we propose the optimum conditions for obtaining probe shaped deposits, where both the diffusion and reduction control the process.

2 Model and Method for the Simulation

2.1 Model

The diffusion-adsorption-reduction model is assumed for the consumption of propargyl alcohol. Propargyl alcohol, denoted by PA below, diffuses from the bulk of the solution to cathode/solution interface. It adsorbed on the cathode surface following to the Langmuir's isotherm and reduced to the other substance on the cathode. The coverage by the reduction product is assumed to be low and negligible as compared with that of PA. The details on the model were described in the previous paper,⁹⁾ and only the equations derived from the model and used in this paper are described below.

The diffusion rate is given by

$$j_{\text{dif,A}} = -D_A \text{grad} (C_A) \quad (1)$$

where D_A is the diffusion coefficient of PA and C_A is the concentration of PA. The reduction rate is given by

$$v_{\text{red}} = k_r \theta \exp(-b_A E) \quad (2)$$

where k_r is the rate constant of reduction, E is the electrode potential and b_A is the factor of potential dependence and θ is the surface coverage by PA. Adsorption/desorption is at equilibrium and the following equation is given,

$$k_{\text{ad}} C_{\text{Al}} (1 - \theta) = k_{\text{des}} \theta \quad (3)$$

where k_{ad} is the rate constant of adsorption, k_{des} the rate constant of desorption, and C_{Al} is the concentration of PA at the cathode/solution interface. The equation (3) is converted to

$$\theta = 1 / (1 + K_A / C_{\text{Al}}) \quad (4)$$

where $K_A = k_{\text{des}} / k_{\text{ad}}$.

In the steady state, the rate of reduction is equal to the rate of diffusion.

$$j_{\text{dif,A}} = v_{\text{red}} \quad (5)$$

The symbols and their dimensions are noted in the list of symbols.

2.2 Method of Simulation

The geometric configuration of the micropattern and the boundary conditions assumed for the calculation are same to those shown in the previous paper.⁹⁾ This is a

Fig. 1 Geometric configuration, bird's-eye view, of a micro-pattern and boundary conditions for the simulation: $r_1 = 30 \mu\text{m}$, $r_2 = 60 \mu\text{m}$, $z_2 = 5$ to $50 \mu\text{m}$.

concentration problem in cylindrical polar coordinate, (r, ϕ, z) , but it reduces to a problem of two dimensional coordinate (r, z) , on the assumption that the concentration is symmetric in all r direction, that is, the concentration does not depend on ϕ . The cylinder, the plain, the coordinate and the boundary conditions used for the calculations are shown in Fig.1. This figure shows the condition that the holes are filled uniformly with nickel deposit to the equal level of the resist surface. The radius of the hole, r_1 , is $30 \mu\text{m}$ and the radius of the cylinder, r_2 , is $60 \mu\text{m}$. The thickness of the diffusion layer, z_2 that is the height of the cylinder is changed from 5 to $50 \mu\text{m}$.

A differential equation written as

$$\partial (r \partial C_A / \partial r) / \partial r + \partial (r \partial C_A / \partial z) / \partial z = 0 \quad (6)$$

is solved numerically by boundary element method with adequate boundary conditions, and the rate of diffusion is calculated by equation (1).

In the previous paper,⁹⁾ the differential equation was mistyped as $(\partial^2 C_A / \partial r^2) / r + (\partial^2 C_A / \partial z^2) = 0$, and the results shown in the previous paper were also obtained by solving equation (6).

On the surface of the cathode, coordinate of which is given by (r, z) , the rate of diffusion of PA poured onto the surface is equal to the rate of reduction of PA. From equation (2) and (5)

$$j_{\text{dif,A}} (r, z) = k_r \theta (r, z) \exp[-b_A E (r, z)] \quad (7)$$

The ratio of the rate at (r, z) to that at the center of cathode surface $(0, z_0)$ is

$$j_{\text{dif,A}} (r, z) / j_{\text{dif,A}} (0, z_0) = \theta (r, z) / \theta (0, z_0) \quad (8)$$

under the condition that the potential difference is negligible, *i.e.* $E (r, z) = E (0, z_0)$.

This is an important relation to judge whether the result of calculation is reasonable or not (*cf.* the Appendix). It was found that concentration of PA at cathode/solution interface, C_{Al} , must vary properly along the interface to satisfy equation (8).⁹⁾ In the simulations, the optimum functions that represent the proper variations of C_{Al} along the interface are given for the boundary conditions

to solve equation (6).

The ratio of current density due to nickel deposition is given by⁹⁾

$$\frac{i_{\text{Ni}}(r,z)/i_{\text{Ni}}(0,z_0)}{C_{\text{M1}}(r,z)/C_{\text{M1}}(0,z_0)} = \frac{[1 - \theta(r,z)]}{[1 - \theta(0,z_0)]} \quad (9)$$

Under the conditions that $C_{\text{M1}}(r,z)/C_{\text{M1}}(0,z_0)$ is nearly unity (*cf.* Appendix) the current ratio is simply given by

$$i_{\text{Ni}}(r,z)/i_{\text{Ni}}(0,z_0) = [1 - \theta(r,z)]/[1 - \theta(0,z_0)] \quad (10)$$

The current ratio, that corresponds the current distribution of nickel deposition, is evaluated from equation (10).

It is important for obtaining probe shaped deposits that the deposits have high aspect ratios, as far as possible, in the initial stage of electrodeposition, because the growth of the deposits tend to be isotropic as they grow.^{9),12)} In this paper, the simulations are done for the flat surface, where the hole is filled uniformly with the deposit to the equal level of the resist surface.

Precise conditions for the calculation were described in the previous paper.⁹⁾

3 Results and Discussion

All of the simulated results are those that are obtained with the optimum C_{A1} functions (*cf.* Appendix), that is, with the boundary conditions that give the reasonable answers satisfying equation (8). The following values⁹⁾ are also used in this paper.

$$v_{\text{red}} = 1.14 \times 10^{-15} \theta \exp(-16.8 E) \text{ mol cm}^{-2} \text{ s}^{-1}, \\ K_{\text{A}} = 1.0 \times 10^{-9} \text{ mol cm}^{-3}, D_{\text{A}} = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

C_{A1} functions used in this paper are combinations of r_0^n and $\exp(ar_0)/\exp(a)$ instead of the combinations of r^n , $\exp(ar)$ and $\tan(br)$,⁹⁾ where r_0 is r/r_1 , because the former functions were easier for finding out the optimum function than the latter. The results obtained with the former and the later differed little, because both functions were optimized. The software used for the calculations was Macsyma PDEase2D™ (Macsyma Inc).

3.1 Effect of the cathode potential

The growing habit of the deposit depended on the electrode potential. At -0.80 V, the growth of the deposit in the horizontal direction was suppressed and the shape of the deposit became round.⁹⁾ On the other hand, the suppression of the growth in the horizontal direction was not obvious and rather flat deposits were obtained at -0.85 V.⁹⁾ The causes why the growing habit depends on the cathode potential are discussed below.

The shape control function of PA, its dependence on the cathode potential, was simulated at 1.8×10^{-7} mol cm^{-3} of C_{A0} , the bulk concentration of PA, and at $50 \mu\text{m}$ of δ ($=z_2$), the thickness of the diffusion layer. Figure 2 shows the diffusion rate, $j_{\text{dif,A}}(r,0)$, of PA which comes normally to the cathode surface, calculated at -0.80 V and -0.85 V. These results are the same as those reported in the previous paper,⁹⁾ which were obtained with C_{A1} functions different from these used in this paper. As

Fig. 2 The diffusion rate of PA flew onto the cathode surface and the maximum reduction rate calculated at two different potentials: diffusion rates, $j_{\text{dif,A}}(r,0)$, are simulated under the conditions of C_{A0} , 1.8×10^{-7} mol cm^{-3} ; δ , $50 \mu\text{m}$; “●”, at -0.80 V; “▲”, at -0.85 V vs. Ag/AgCl with C_{A1} functions. “●”, $C_{\text{A1}}(r,0) = 2.36 \times 10^{-9} [1 + (4r_0^2 + 4r_0^3 + 7r_0^5 + 7r_0^6) \exp(0.5 r_0)/\exp(0.5)]$ mol cm^{-3} . “▲”, $C_{\text{A1}}(r,0) = 3.80 \times 10^{-10} [1 + (4r_0^2 + r_0^4 + r_0^6 + 15r_0^{20} + 25r_0^{30}) \exp(6r_0)/\exp(6)]$ mol cm^{-3} , where $r_0 = r/r_1$. The maximum reduction rates, $v_{\text{red}}(\theta=1)$ are calculated from $1.14 \times 10^{-15} \exp(-16.8 E)$: “a” at -0.80 V, “b” at -0.85 V.

C_{A1} functions used in both papers were the optimum functions, the same results were obtained. The line labeled with “●” is the result calculated at -0.80 V, and that labeled with “▲” is the result at -0.85 V. The spike shown in the vicinity of the edge of the cathode surface is considered to be due to the calculation error and is neglected. At -0.85 V, the variation is gradual in the range of r less than $20 \mu\text{m}$, but it becomes steep beyond this region. This result is nearly the same as that obtained with $C_{\text{A1}}(r,0) = 0$, which corresponds to the variation of diffusion rate under the condition of diffusion limiting. On the other hand, the diffusion rate is low and its variation with r is gradual in the whole region of r at -0.80 V, showing the result far from diffusion limiting.

Figure 2 also shows the reduction rate when the coverage by PA is unity, *i.e.* $v_{\text{red}}(\theta=1)$, that corresponds to the maximum reduction rate at each potential. At -0.85 V, $j_{\text{dif,A}}(r,0)$ is far lower than $v_{\text{red}}(\theta=1)$ except for the region in the vicinity of the edge. At -0.80 V, on the other hand, difference between $j_{\text{dif,A}}(r,0)$ and $v_{\text{red}}(\theta=1)$ is small, especially in the range of r between 20 and $30 \mu\text{m}$. The value of $j_{\text{dif,A}}(r,0)/v_{\text{red}}(\theta=1)$ is equal to θ as derived from equation (7). It is shown by this figure that θ is higher and its variation with r is more gradual at -0.80 V as compared with the result obtained at -0.85 V. The differences in θ and variation of θ with r , which are very important factors that determine the shape control function, are closely related $j_{\text{dif,A}}(r,0)$ and $v_{\text{red}}(\theta=1)$.

The shape control function of PA depends on the diffusion of PA, rate of which is different at position to position. It is considered that the diffusion flux, which comes around to the cathode/solution interface from the diffusion layer above the resist/solution interface, plays an important role. The cause of the difference shown in Fig. 2 is considered as follows.

At the beginning of the electrolysis, the interfacial concentration of PA, C_{A1} , is constant and equal to C_{A0} at every point of cathode/solution interface. C_{A1} becomes lower as the electrolysis proceeds until the steady state is established. At the edge of the cathode surface, larger amount of PA is diffused from the diffusion layer above the resist/solution interface, as compared with the interior of the surface. The extent in lowering of C_{A1} is smaller at the edge than in the interior. This cause the variation of C_{A1} along the interface, and this variation of C_{A1} also influences the concentration, C_A , in the diffusion layer. The variation of C_A makes the flux of PA to direct toward the interior of the surface, degree of which depends on the electrode potential, *i.e.* the reduction rate of PA.

When the reduction rate is high, the most part of PA that comes around to the vicinity of the edge is consumed by the reduction and the flux of PA is concentrated in the vicinity of the edge. When the reduction rate is low, PA that comes to the edge of the cathode remains unreduced, and large part of PA must go toward the interior of the surface. The case at -0.80 V is the example that the reduction rate is low and the case of -0.85 V is the example of high reduction rate.

The difference in the flux distribution results the difference in the PA coverage on the cathode surface, or vice versa, that is considered to be the cause of different growing habit obtained at different cathode potentials. How the potential affect the function of PA is discussed further.

Variations of $\theta(r,0)$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ along the cathode surface calculated at several potentials are shown in Fig. 3. These values are obtained from the C_{A1} functions and equation (4). The values at -0.80 V and -0.85 V are the same as reported in the previous paper.⁹⁾ The variation of $\theta(r,0)$ reflects the variation of diffusion rate, $j_{\text{dif},A}(r,0)$, and $[1-\theta(r,0)]/[1-\theta(0,0)]$ reflects the current ratio of nickel electrodeposition, as indicated by equation (8) and equation (10). At each potential, $\theta(r,0)$ is nearly unity at r of $30 \mu\text{m}$. At -0.85 , -0.825 , and -0.80 V, it becomes lower as r decreases, and it becomes higher as the potential becomes less negative. At the potential less negative than -0.78 V, $\theta(r,0)$ approaches to unity, that is, $j_{\text{dif},A}(r,0)$ approaches to v_{red} ($\theta=1$) in the whole range of r . $[1-\theta(r,0)]/[1-\theta(0,0)]$ decreases as r becomes larger, and it decreases as the potential becomes less negative in the potential range between -0.80 and -0.85 V. In the potential range less negative than -0.78 V, $[1-\theta(r,0)]/[1-\theta(0,0)]$ becomes higher again. At the potential range less negative than -0.78 V, the variation of $\theta(r,0)$ is so small that $[1-\theta(r,0)]/[1-\theta(0,0)]$ results in relatively small variation. In other words, the electrodeposition of nickel is strongly inhibited in the whole range of r . At -0.85 , -0.825 and -0.80 V, the ratio of $[1-\theta(r,0)]$ at the edge to that at the center, *i.e.* $[1-\theta(r_1,0)]/[1-\theta(0,0)]$, is nearly same. But $[1-\theta(r,0)]/[1-\theta(0,0)]$ is lower and its variation with r is more gradual at less negative potential in almost whole region of r . The reason is that the distribution of PA diffusion flux is less concentrated

Fig. 3 Variation of $\theta(r,0)$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ along the cathode surface calculated under the following conditions ; C_{A0} , $1.8 \times 10^{-7} \text{ mol cm}^{-3}$; δ , $50 \mu\text{m}$; E; $\blacklozenge$, -0.77 V; $\blacktriangle$, -0.78 V; $\circ$, -0.80 V; $\diamond$, -0.825 V; $\triangle$, -0.85 V vs. Ag/AgCl.

in the vicinity of the cathode edge and $\theta(r,0)$ varies gradually in the whole range of r at less negative potential.

Both of the experimental and the simulated results obtained at -0.85 V show that the shape control function of PA is not obvious,⁹⁾ though the value of $[1-\theta(r,0)]/[1-\theta(0,0)]$ at -0.85 V is nearly the same to that at -0.80 V. The reason is considered to be that the flat part of $[1-\theta(r,0)]$ influence the growing habit at -0.85 V. The condition of the gradual variation of $[1-\theta(r,0)]$ as in the case of electrodeposition at -0.80 V is preferable for suppressing the growth in horizontal direction.

In the case of electrodeposition at -0.85 V, the process is strongly controlled by the diffusion of PA, as described above. The difference in the shape control function of PA at different potentials is considered to relate to what extent the diffusion of PA control the diffusion-adsorption-reduction process. The factors that reflect to what extent the diffusion of PA control the process, and to what extent the reduction of PA control the process, are introduced. They are $j_{\text{av}}/j_{\text{lim}}$ and $j_{\text{av}}/v_{\text{red}}$ ($\theta=1$). The average value of $j_{\text{dif},A}(r,0)$, j_{av} , is calculate as follows. The total amount of PA that pours onto the cathode surface is obtained by the integration, *i.e.* $\int_0^{2\pi} \int_0^{r_1} j_{\text{dif},A}(r,0) r dr d\phi$, that is equal to $j_{\text{av}} \pi r_1^2$. Then j_{av} is given by

$$j_{\text{av}} = 2\pi \left[\int_0^{r_1} j_{\text{dif},A}(r,0) r dr \right] / \pi r_1^2 \quad (11)$$

where $j_{\text{dif},A}(r,0)$ is the result obtained by the simulation

Fig. 4 Potential dependence of j_{av}/j_{lim} and j_{av}/v_{red} ($\theta=1$) calculated under the following conditions: C_{A0} , 1.8×10^{-7} mol cm^{-3} ; δ , 50 μm : $\circ$, j_{av}/j_{lim} ; $\triangle$, j_{av}/v_{red} ($\theta=1$).

and $j_{dif,A}(r,0)$ r is integrated in the r range from 0 to r_1 . The average value of $j_{dif,A}(r,0)$ when the diffusion rate is limiting is denoted by j_{lim} and obtained by the simulation by setting the boundary value of $C_{A1}(r,0)$ to be 0, and calculated from equation (11). The rate of reduction of PA at $\theta=1.0$, v_{red} ($\theta=1$), is calculate from equation (2). The process is essentially controlled by the diffusion, when j_{av}/j_{lim} is nearly unity. The process is essentially controlled by the cathodic reduction, when j_{av}/v_{red} ($\theta=1$) is nearly unity.

Figure 4 shows the potential dependence of j_{av}/j_{lim} and j_{av}/v_{red} ($\theta=1$), j_{av}/j_{lim} equals to 1.0 at -0.85 V showing that the diffusion strongly control the process, *i.e.* diffusion limiting condition. The value of j_{av}/j_{lim} decreases as the potential becomes less negative showing that the diffusion controls less strongly the process. The value of j_{av}/v_{red} ($\theta=1$) is as low as 0.47 at -0.85 V and increases as the potential becomes less negative. It approaches unity at -0.77 V. Unity of j_{av}/v_{red} ($\theta=1$) indicates that the reduction reaction control prevails the diffusion control. As described above, the shape control function of PA is best at -0.80 V, where both of the diffusion and reduction control the process.

3. 2 Effect of the thickness of diffusion layer

PA does not work well as a shape control agent at -0.85 V, when the thickness of the diffusion layer is 50 μm and the bulk concentration of PA is 1.8×10^{-7} mol cm^{-3} . The effect of the thickness of diffusion layer, δ , was simulated under the following conditions; the bulk PA concentration of 1.8×10^{-7} mol cm^{-3} and the electrode potential of -0.85 V. The variation of $\theta(r,0)$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ calculated at several δ are shown in Fig. 5. The coverage, $\theta(r,0)$, becomes higher as δ is decreased and approaches unity at δ of 5 μm . The effect of δ is considered as follows.

The diffusion rate is higher with thinner diffusion layer. It is very lower than v_{red} ($\theta=1$) in wide range of r as shown in Fig. 2 at δ of 50 μm . As δ decreases, the diffusion rate becomes higher and approaches to v_{red} ($\theta=1$).

The current ratio, $[1-\theta(r,0)]/[1-\theta(0,0)]$, is lower and its variation with r is more gradual at less δ , in δ range between 50 and 10 μm , but it becomes higher and approaches unity as δ decreases in δ range less than 10 μm . The optimum δ for obtaining a round deposit is be-

Fig. 5 Variation of $\theta(r,0)$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ along the cathode surface calculated under the following conditions; C_{A0} , 1.8×10^{-7} mol cm^{-3} ; electrode potential, -0.85 V vs. Ag/AgCl; δ ; $\blacklozenge$, 5 μm ; $\blacktriangle$, 10 μm ; $\circ$, 15 μm ; $\diamond$, 25 μm ; $\triangle$, 50 μm .

Fig. 6 Dependence of j_{av}/j_{lim} and j_{av}/v_{red} ($\theta=1$) on the thickness of diffusion layer calculated under the following conditions: C_{A0} , 1.8×10^{-7} mol cm^{-3} ; E, -0.85 V vs. Ag/AgCl: $\circ$, j_{av}/j_{lim} ; $\triangle$, j_{av}/v_{red} ($\theta=1$).

tween 10 and 15 μm .

Figure 6 shows the variation of j_{av}/j_{lim} and j_{av}/v_r ($\theta=1$) with δ . j_{av}/j_{lim} is unity at δ of 50 μm , and it becomes lower as δ is decreased. j_{av}/v_r ($\theta=1$) is as low as 0.47 at δ of 50 μm and it becomes higher as δ is decreased and approaches unity at δ of 5 μm . The results shown in Fig. 6 indicate that the process is strongly controlled by the diffusion of PA at δ of 50 μm and that the effect of the diffusion becomes weak and the reduction reaction control becomes strong as δ decreases.

The shape control function is considered to be best at δ between 10 and 15 μm under the condition; at -0.85 V and C_{A0} of 1.8×10^{-7} mol cm^{-3} . In this condition, both the diffusion and reduction control the process.

Fig. 7 Variation of $[1 - \theta(r,0)]/[1 - \theta(0,0)]$ at several PA concentrations calculated under the following conditions: δ , 50 μm ; C_{A0} ; $\blacktriangle$, $9.0 \times 10^{-8} \text{ mol cm}^{-3}$; $\triangle$, $1.8 \times 10^{-7} \text{ mol cm}^{-3}$; $\bullet$, $3.6 \times 10^{-7} \text{ mol cm}^{-3}$; $\circ$, $9.0 \times 10^{-7} \text{ mol cm}^{-3}$.

3. 3 Effect of the concentration of PA

From the results shown above, PA works well as a shape-controlling agent, when both of the diffusion and the reduction control the process. In these cases, the coverage at the center of the cathode, $\theta(0,0)$, is nearly 0.75.

The current ratios calculated under the condition, $\theta(0,0)$ of 0.75 and δ of 50 μm , at several bulk concentration of PA are compared in Fig. 7. The current ratio becomes lower and its variation more gradual as C_{A0} becomes higher, showing that PA works better as a shape control agent at higher bulk concentration.

The potential that make $\theta(0,0)$ to be 0.75 changes with C_{A0} , because $j_{\text{dif},A}(0,0)$ changes with C_{A0} . The electrode potential is calculated by the following equation derived from Eq.(2).

$$E = -\ln[j_{\text{dif},A}(0,0)/(1.14 \times 10^{-15} \times 0.75)]/16.8 \quad (12)$$

The calculated potential that makes $\theta(0,0)$ to be 0.75 is as follows.

C_{A0}	E
$0.9 \times 10^{-7} \text{ mol cm}^{-3}$	-0.76 V
$1.8 \times 10^{-7} \text{ mol cm}^{-3}$	-0.80 V
$3.6 \times 10^{-7} \text{ mol cm}^{-3}$	-0.84 V
$9.0 \times 10^{-7} \text{ mol cm}^{-3}$	-0.89 V

It is concluded from the results described above that PA works better as a shape control agent at higher bulk concentration. The appropriate potential shifts to more negative as the bulk concentration becomes higher. The current allotted to nickel electrodeposition is evaluated to be 15 mA cm^{-2} at -0.80 V and 60 mA cm^{-2} at -0.89 V in the absence of the additive.⁸⁾ The current density used for nickel deposition at the center of the cathode is calculated to be 3.8 mA cm^{-2} at -0.80 V and 15 mA cm^{-2} at -0.89 V, when $\theta(0,0)$ equals 0.75. The electrodeposition at higher concentration of PA and at more negative potential is profitable, also in view of productivity.

The reduction product of PA, the effect of which was neglected in this paper, might play an important role as

the concentration of PA becomes higher. More reliable results will be obtained by considering the effect of the reduction product.

4 Conclusions

The effects of electrode potential, the thickness of diffusion layer and the bulk concentration of propargyl alcohol on the shape control function of propargyl alcohol were investigated. The following conclusions were obtained.

- 1) There are the optimum potential and the thickness of diffusion layer to form probe shaped deposition. In the optimum conditions, both of the diffusion and the reduction reaction of propargyl alcohol control the diffusion-adsorption-reduction process.
- 2) The simulation showed that the shape can be controlled better at higher bulk concentration of propargyl alcohol. And the electrodeposition at higher bulk concentration and at more negative potential is profitable in view of productivity.

It is expected that this investigation improves the understanding of electrodeposition in micro scale to make progress in microfabrication technology.

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Appendix

Adequate and optimum C_{A1} functions

As described above, the calculations were conducted with C_{A1} -functions that were used for the boundary conditions at cathode/solution interface. The calculated results were not physically acceptable, if used C_{A1} -functions were not adequate. Figure A-1 shows two cases of $C_A(r,0)$ obtained by the calculations; one is that C_{A1} -function was not adequate and the other is that C_{A1} -function was adequate. The range less than 30 μm corresponds to the cathode/solution interface and the range more than 30 μm corresponds the resist/solution interface. The curve

Fig. A-1 Variation of $C_A(r,0)$ along the cathode/solution and resist/solution interface calculated in two cases of C_{A1} -functions: "a", $C_{A1}(r,0) = 2.36 \times 10^{-9} \text{ mol cm}^{-3}$, "b", $C_{A1}(r,0) = 2.36 \times 10^{-9} [1 + (4r_0^2 + 4r_0^3 + 7r_0^5 + 7r_0^6) \exp(0.5r_0)/\exp(0.5)] \text{ mol cm}^{-3}$.

denoted by "a" is the result when a constant value of $2.36 \times 10^{-9} \text{ mol cm}^{-3}$ is used for C_{A1} -function. The horizontal line in the region less than $30 \mu\text{m}$ is the given boundary value, and the curve in the region more than $30 \mu\text{m}$ is the calculated result. This result shows that $C_A(r,0)$ changes abruptly at $r = 30 \mu\text{m}$, *i.e.* at the boundary of two kinds of interface, that is physically not acceptable. The curve denoted by "b" is the result when the following equation is used for C_{A1} -function.

$$C_{A1}(r,0) = 2.36 \times 10^{-9} [1 + (4r_0^2 + 4r_0^3 + 7r_0^5 + 7r_0^6) \exp(0.5r_0)/\exp(0.5)]$$

where $r_0 = r/r_1$. This curve varies continuously and smoothly at $30 \mu\text{m}$, showing the result is physically acceptable. A C_{A1} -function that gives a physically acceptable result is called an adequate C_{A1} -function.

Equation (8) must be satisfied, when the result of calculation is reasonable. Among the adequate C_{A1} -functions, a function that gives the result satisfying equation (8) is called the optimum C_{A1} -function. Figure A-2 shows two examples obtained with an optimum C_{A1} -function. The ratios, $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ and $C_f(r,0)$, are plotted vs. r , where $C_f(r,0)$ is,

$$C_f(r,0) = \{1/[1 + K_A/C_A(r,0)]\} / \{1/[1 + K_A/C_A(0,0)]\} \quad (\text{A-1})$$

This is equal to $\theta(r,0)/\theta(0,0)$ in the region of cathode/solution interface. $C_f(r,0)$ in the region of resist/solution interface has no physical meaning, but its smooth variation at the boundary between two kinds of interface, that is at r of $30 \mu\text{m}$ in this case, indicate that used C_{A1} -function is adequate one. The value $\theta(r,0)/\theta(0,0)$ is directly obtained from the given C_{A1} -function and $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ is the result obtained from the calculation. $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ is nearly equal to $\theta(r,0)/\theta(0,0)$ except for the spike which is shown in the vicinity of $r = 30 \mu\text{m}$

Fig. A-2 Variation of $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ and $C_f(r,0)$ along the cathode/solution and the resist/solution interface calculated with two optimum C_{A1} functions: "a" and "b"; variation of $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ and $C_f(r,0)$, respectively, calculated with $C_{A1}(r,0) = 2.36 \times 10^{-9} [1 + (4r_0^2 + 4r_0^3 + 7r_0^5 + 7r_0^6) \exp(0.5r_0)/\exp(0.5)] \text{ mol cm}^{-3}$. "c" and "d"; variation of $j_{\text{dif},A}(r,0)/j_{\text{dif},A}(0,0)$ and $C_f(r,0)$, respectively, calculated with $C_{A1}(r,0) = 3.80 \times 10^{-10} [1 + (4r_0^2 + r_0^4 + r_0^6 + 15r_0^{20} + 25r_0^{30}) \exp(6r_0)/\exp(6)] \text{ mol cm}^{-3}$.

and considered to be due to calculation error.

All of the results shown in this paper are those obtained with the optimum C_{A1} -functions.

Mass transport of metal ions

Influence of mass transport of nickel ions on the nickel electrodeposition in the presence of an additive was simulated. The differential equation

$$\partial (r \partial C_M / \partial r) / \partial r + \partial (r \partial C_M / \partial z) / \partial z = 0 \quad (\text{A-2})$$

is solved numerically, where C_M is the concentration of nickel ion. The rate of mass transport of nickel ions in the diffusion layer, including diffusion and migration, is given by

$$j_M = -[D_M/(1-t_+)] \text{ grad } C_M$$

$$D_M = (z_+u_+D_- - z_-u_-D_+) / (z_+u_+ - z_-u_-)$$

$$t_+ = z_+u_+ / (z_+u_+ - z_-u_-)$$

where z_+, u_+ and D_+ is the valence, the mobility and the diffusion coefficient of cation, z_-, u_- and D_- is the valence, the mobility and the diffusion coefficient of anion, respectively.¹³⁾ The value of D_M is evaluated to be $0.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, considering the concentration and temperature dependence of equivalent conductance of NiSO_4 solution.¹⁴⁾

The same geometric configuration and similar boundary conditions as shown in Fig.1 are considered. The boundary conditions including the concentration of nickel ion in the bulk of the solution, C_{M0} , and interfacial concentration, C_{M1} , are as follows.

$$C_{A0} = 1.8 \times 10^{-7} \text{ mol cm}^{-3}, C_{M0} = 1.0 \times 10^{-3} \text{ mol cm}^{-3}$$

$$C_{A1}(r,0) = 3.8 \times 10^{-10} [1 + (4r_0^2 + r_0^4 + r_0^6 + 15r_0^{20} + 25r_0^{30}) \exp(6r_0)/\exp(6)]$$

$$C_{M1}(r,0) = 9.0 \times 10^{-4} [1 + (0.002r_0^{1.1} + 0.05r_0^2 + 0.005r_0^3) \exp(0.5r_0)/\exp(0.5)]$$

Fig. A-3 Variations of $i_{\text{Ni}}(r,0)/i_{\text{Ni}}(0,0)$, $C_{M1}(r,0)[1-\theta(r,0)]/C_{M1}(0,0)[1-\theta(0,0)]$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ calculated under the following conditions: C_{A0} , $1.8 \times 10^{-7} \text{ mol cm}^{-3}$; C_{M0} , $1.0 \times 10^{-3} \text{ mol cm}^{-3}$; δ , $50 \mu\text{m}$; $C_{A1}(r,0) = 3.80 \times 10^{-10} [1 + (4r_0^2 + r_0^4 + r_0^6 + 15r_0^{20} + 25r_0^{30}) \exp(6r_0)/\exp(6)]$; $C_{M1}(r,0) = 9 \times 10^{-4} [1 + (0.002r_0^{1.1} + 0.05r_0^2 + 0.005r_0^3) \exp(0.5r_0)/\exp(0.5)]$. "a", $i_{\text{Ni}}(r,0)/i_{\text{Ni}}(0,0)$; "b", $C_{M1}(r,0)[1-\theta(r,0)]/C_{M1}(0,0)[1-\theta(0,0)]$; "c", $[1-\theta(r,0)]/[1-\theta(0,0)]$.

$C_{M1}(r,0)$ is optimum function that gives the result satisfying Eq. (9).

The simulated results are shown in Fig. A-3, where $i_{Ni}(r,0)/i_{Ni}(0,0)$ and $[1-\theta(r,0)]/[1-\theta(0,0)]$ and $C_{M1}(r,0)[1-\theta(r,0)]/C_{M1}(0,0)[1-\theta(0,0)]$ are compared. $[1-\theta(r,0)]/[1-\theta(0,0)]$ and $C_{M1}(r,0)[1-\theta(r,0)]/C_{M1}(0,0)[1-\theta(0,0)]$ are calculated directly from the given values of $C_{A1}(r,0)$ and $C_{M1}(r,0)$, and $i_{Ni}(r,0)/i_{Ni}(0,0)$ is obtained by solving Eq. (A-2). Three curves coincide each other well, showing that equation (9) and (10) hold. Therefore, $[1-\theta(r,0)]/[1-\theta(0,0)]$ approximates to the current ratio of nickel deposition. The reason is that the ratio, $C_{M1}(r,0)/C_{M1}(0,0)$, is nearly unity, i.e. 1.06. In this case, the current density at the center of the cathode, $i_{Ni}(0,0)$, is calculated to be 48 mA cm^{-2} .

The calculation showed that the difference between $[1-\theta(r,0)]/[1-\theta(0,0)]$ and $C_{M1}(r,0)[1-\theta(r,0)]/C_{M1}(0,0)[1-\theta(0,0)]$ became large as $i_{Ni}(0,0)$ became higher. The difference was small but apparent when $i_{Ni}(0,0)$ was about 97 mA cm^{-2} . Under the simulation conditions in this paper, the maximum current density allotted to nickel electrodeposition is calculated to be about 22 mA cm^{-2} , that is, the current density at -0.85 V and $\theta(0,0)=0.72$. The approximation that $[1-\theta(r,0)]/[1-\theta(0,0)]$ represents the current ratio of nickel electrodeposition is reliable under the conditions of simulation done in this paper, though the effect of mass transfer of nickel ions should be taken into consideration under the conditions of higher current densities, for example higher than 100 mA cm^{-2} .

List of Symbols

b_A ; potential depending coefficient of PA reduction rate, V^{-1}

$C_A, C_A(r,z)$; concentration of PA in diffusion layer, mol cm^{-3}

C_{A0} ; concentration of PA in the bulk of the solution, mol cm^{-3}

$C_{A1}, C_{A1}(r,z)$; concentration of PA at the cathode/solution interface, mol cm^{-3}

C_{M0} ; concentration of nickel ion in the bulk of the solution, mol cm^{-3}

C_{M1} ; concentration of nickel ion at the solution/cathode interface, mol cm^{-3}

D_A ; diffusion coefficient of PA, $\text{cm}^2 \text{ s}^{-1}$

D_M ; mass transport coefficient of metal ion, $\text{cm}^2 \text{ s}^{-1}$

D^+, D^- ; diffusion coefficient of cation or anion, $\text{cm}^2 \text{ s}^{-1}$

$E, E(r,z)$; electrode potential, $V_{\text{vs. Ag/AgCl}}$

j_{av} ; average value of $j_{\text{dif},A}(r,0)$ calculated from equation (11), $\text{mol cm}^{-2} \text{ s}^{-1}$

$j_{\text{dif},A}, j_{\text{dif},A}(r,z)$; diffusion rate of PA, $\text{mol cm}^{-2} \text{ s}^{-1}$

j_{lim} ; diffusion limited value of j_{av} , $\text{mol cm}^{-2} \text{ s}^{-1}$

j_M ; rate of metal deposition, $\text{mol cm}^{-2} \text{ s}^{-1}$

k_{ads} ; rate constant of adsorption of PA, cm s^{-1}

k_{des} ; rate constant of desorption of PA, $\text{mol cm}^{-2} \text{ s}^{-1}$

k_r ; rate constant of PA reduction, $\text{mol cm}^{-2} \text{ s}^{-1}$

K_A ; equilibrium constant of adsorption, mol cm^{-3}

u^+, u^- ; mobility of cation or anion, $\text{cm}^2 \text{ mol J}^{-1} \text{ s}^{-1}$

v_{red} ; rate of reduction of PA; $\text{mol cm}^{-2} \text{ s}^{-1}$

z^+, z^- ; valence of cation or anion

δ ; thickness of the diffusion layer, cm in the calculation

$\theta, \theta(r,z)$; coverage of PA on the cathode surface

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