Theoretical studies of displacement deposition of nickel into porous silicon with ultrahigh aspect ratio
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Abstract
A model is developed to address the uniformity of displacement deposition of nickel inside porous silicon with an ultrahigh aspect ratio as high as 200. The nickel distribution is treated as a current distribution issue as in electrodeposition. It is shown that the deposition distribution along the pore depth exhibits a strong dependence on a polarization parameter ξ. High values of ξ correspond to mass transport limitations and lead to non-uniform distributions, whereas small ξ values, representing interfacial reaction control, produce uniform distributions. Non-uniform deposition primarily occurs at an initial stage in which the reaction is dominated by mass transfer. As the deposition process continues, the deposition rate drops to a low value, and the deposition uniformity shifts from Ni2+ mass transport limitations to its interfacial reaction control, leading to uniform Ni2+ concentration and deposition rate distributions. It is predicted that the non-uniformity at the initial stage could be remedied by increasing the bulk concentration of the nickel ions and decreasing the plating bath pH. In addition, the uniformity of the deposition distribution can be significantly improved by introducing inhibiting additive coumarin to the plating solution.

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Keywords: Displacement deposition; Porous silicon; Current distribution; Nickel plating; Deposition uniformity

1. Introduction
Metal deposition into porous silicon (PS) is of great significance for the improvement of electroluminescence of the PS by forming a good electrical contact [1–12,15–17]. It also finds use in fabrication of highly sensitive surface-enhanced Raman scattering substrates [13,14]. Recently, this technique was explored as a means to create a substrate impedance architecture for microwave isolation in mixed-signal integrated circuits [18]. Such architecture can be fabricated by etching a porous region of pore size 1–2 μm and depth ∼200 μm on a Si substrate, followed by depositing metal into the pores. The deposited metal must be uniformly distributed inside the pores.

Displacement deposition is the most promising process for such deep pores based on its unlimited throwing power under uniform concentration distribution of depositing species [19]. However, for pores with an aspect ratio up to 200, uniform deposition from the pore top to bottom is not readily obtained because of the restricted mass transport and consequent non-uniform concentration distribution of the depositing species [20].

A number of experimental studies have been carried out to investigate deposition of metal into the PS. Hamm et al. made extensive investigation in this field [1–3,5,10–12]. Herino reviewed a wide variety of processes used for this deposition [19]. The review indicates that pore filling is not readily achieved and most of the investigated deposition processes lead to a pronounced deposit gradient profile. Usually, the deposited PS reported in literature has a porous layer thickness of 0.5–15 μm with maximum deposition depth being 1.3 μm. Most of the studies were directed toward the influence of bath chemistry on the effectiveness of the plating and deposition mechanism. Apparently, the current technologies cannot meet the challenge of plating the PS with depth of 200 μm and an aspect ratio of ∼200.

Although theoretical and experimental studies of deposition distribution for similar geometries, such as through-holes [20–28] and trenches or vias [20,29–47], are abundant, the nature
of the deposition process for the geometry in the present study is vastly different from those in literature. In through-hole plating, concerns on mass transport deficiency are unwarranted since the inside of the holes is accessible to agitation because of their relatively large dimensions; the non-uniformity caused by reactant depletion is readily avoided by adequate agitation [20,21]. In the case of copper plating for on-chip interconnection, superconformal bottom-up filling was accomplished by use of multiple additives. The role of the organic additives was described by a diffusion–adsorption leveling theory for a leveler-dominated additives. The role of the organic additives was described by a diffusion–adsorption leveling theory for a leveler-dominated system [32,34–36], or by accelerator or catalyst models for systems with accelerators and suppressors [39–42,44–47]. In either of the models, metal deposition is activation controlled.

For the nickel displacement deposition process studied in this paper, as will be seen, mass transport rate is a very important factor governing the deposition distribution because of ineffectiveness of external agitation in penetrating into the pores of such ultrahigh aspect ratio. In addition, the surface kinetics also influence the plating uniformity as the system mixed potential varies considerably with deposition time.

This paper theoretically addresses the issue of the deposition uniformity assuming that a displacement process is used for nickel deposition into the PS. The nickel distribution is treated as a current distribution issue as in electrodeposition. We derive a model, which takes into account the variation of the interfacial kinetics with time and the consumption of depositing species along their diffusion path, to acquire an in-depth understanding of the dependence of the uniformity of nickel deposition into the PS on the interfacial reaction and diffusion kinetics, and identify approaches to improve the uniformity based on the plating bath chemistry. Moreover, a modified version of models developed by Dukovic and Tobias [48] and Madore et al. [49] is used to explore the applicability of inhibiting additive coumarin to the uniformity issue in the present study.

2. Theory

2.1. Model development

It is assumed that nickel is the metal of choice to deposit the PS. When a piece of porous Si substrate is immersed into a solution containing nickel ions and fluoride but no reducing regent, following electrochemical reactions occur simultaneously at the silicon/solution interface:

- Anodic dissolution:
  \[ \text{Si} + 6\text{F}^- = \text{SiF}_6^{2-} + 4e^- \quad (1) \]

- Cathodic reduction:
  \[ \text{Ni}^{2+} + 2e^- = \text{Ni} \quad (2) \]
  \[ 2\text{H}^+ + 2e^- = \text{H}_2 \quad (3) \]

The uniformity of deposited nickel inside the pores depends on the distribution of the deposition rate of nickel along the pore depth. For the displacement deposition reaction of nickel on the silicon substrate, although there is no current flow through the electrolyte, electrochemical reactions with the donation and acceptance of electrons shown in Eqs. (1)–(3) still occur at the silicon/electrolyte interface. Therefore, the deposition distribution of nickel inside the pores can be treated as a problem of current distribution as in electrochemical systems, with deposition rate being represented by nickel ion diffusion rate or cathodic reduction rate. In electrochemical systems, the current distribution is determined by ohmic potential drop in solution, mass transport, and/or electrode kinetics. However, for the present case of nickel displacement deposition on Si, there is no current flowing through the solution. Electric field effects or potential distribution in the electrolyte corresponding to the current flow is not present. The deposition distribution is then determined by mass transport inside the pores and surface kinetics of nickel depositing reaction. A solution to the diffusion equation can be applied to the inside of the pores. The deposition rate is obtainable from the concentration gradient Ni^{2+} reduction rate. The surface kinetics provides boundary conditions for the diffusion equation.

The cross-section geometry of the pore is shown in Fig. 1(a). Two dimensional coordinate system \((r,y)\) is employed for the mathematical modeling. It is assumed that the plating solution outside the pores is well agitated and mass transport inside the pores occurs only by diffusion because the pores are much deeper than they are wide. Since the pore wall is continually covered by the deposited nickel, its surface area and therefore the system mixed potential vary with time. Thus, the deposition process is operating under non-steady state conditions.

Based on above assumptions, the following non-steady state diffusion equation is solved for Ni^{2+} concentration distribution inside the pores:

\[
\frac{\partial c^*}{\partial t} + D_{\text{Ni}^{2+},i} \frac{\partial}{\partial y} c^* = D_{\text{Ni}^{2+},i} \frac{\partial^2 c^*}{\partial y^2} + \frac{D_{\text{Ni}^{2+},i} n/0}{R_p} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial c^*}{\partial r} \right) = 0 \quad (4)
\]
where the superscript * indicates a dimensionless variable. The variables and parameters were non-dimensionalized by following definitions:

\[ r^* = \frac{r}{R_p}; \quad y^* = \frac{y}{L_p}; \quad t^* = \frac{t}{t_0}; \quad c^* = \frac{c_{Ni^{2+}}^b}{c_{Ni^{2+}}^b} \]  

(5)

The initial and boundary conditions are assumed to be

\[ c^* = 1 \quad \text{at} \quad t^* = 0 \]  

(6)

\[ c^* = 1 \quad \text{at} \quad y^* = 0 \]  

(7)

\[ \frac{\partial c^*}{\partial r^*} = 0 \quad \text{at} \quad r^* = 0 \]  

(8)

At the pore wall surface, the normal diffusion rate is related to \( \text{Ni}^{2+} \) cathodic reduction by

\[ -D_{Ni^{2+}} \frac{c_{Ni^{2+}}^b}{R_p} \frac{\partial c^*}{\partial r^*} = i_{Ni} \frac{nF}{nF} \quad \text{at} \quad r^* = 1 \]  

(9)

The deposition at the pore bottom is negligible with respect to that on the sidewall:

\[ \frac{\partial c^*}{\partial y^*} = 0 \quad \text{at} \quad y^* = 1 \]  

(10)

The \( \text{Ni}^{2+} \) reduction rate \( i_{Ni} \) is related to the surface overpotential by a concentration-dependent Butler–Volmer equation:

\[ i_{Ni} = \left( \frac{c_{Ni^{2+}}^b}{c_{Ni^{2+}}^\infty} \right)^{\gamma} i_0 \left[ \exp \left( \frac{\alpha_e F}{RT} \eta_s \right) - \exp \left( -\frac{\alpha_e F}{RT} \eta_s \right) \right] \]  

(11)

The surface overpotential is a part of the overall overpotential \( \eta \):

\[ \eta = \eta_s + \eta_C \]  

(12)

where \( \eta_C \) is the concentration overpotential and is related to \( c_{Ni^{2+}}^\infty \) by

\[ \eta_C = \frac{RT}{nF} \ln \frac{c_{Ni^{2+}}^\infty}{c_{Ni^{2+}}^b} \]  

(13)

2.2. Bulk \( \text{Ni}^{2+} \) concentration

The bulk concentration \( c_{Ni^{2+}}^b \) of nickel ion \( \text{Ni}^{2+} \) in Eqs. (9) and (13) can be calculated as follows.

When aqueous ammonia is added to adjust the solution pH, \( \text{Ni}^{2+} \) reacts with \( \text{NH}_3(aq) \) to give \( \text{Ni(NH}_3)_n \text{H}_n^{2+} \) complex ion:

\[ \text{Ni}^{2+} + n\text{NH}_3(aq) = \text{Ni(NH}_3)_n \text{H}_n^{2+}, \quad n = 1, 2, \ldots, 6, \]  

(14)

where \( K_n \) denotes the stability constant of \( \text{Ni(NH}_3)_n \text{H}_n^{2+} \) and the factor 10\(^3\) is due to unit conversion.

In practice, the deposition is mostly carried out in a plating bath of pH < 9. The amount of aqueous ammonia added to the bath is less than that needed to form \( \text{Ni(NH}_3)_2^{2+} \). Thus only the formation of \( \text{Ni(NH}_3)_2^{2+} \) needs to be considered. The Eq. (14) is reduced to

\[ K_1 = \frac{c_{\text{Ni(NH}_3)_2^{2+}}}{c_{\text{Ni}^{2+}}^b c_{\text{NH}_3(aq)}} \times 10^3 \]  

(15)

Substituting \( c_0 = c_{\text{Ni}^{2+}}^b \), for \( c_{\text{Ni(NH}_3)_2^{2+}} \), rearranging Eq. (15), and solving for \( c_{\text{Ni}^{2+}}^b \) give

\[ c_{\text{Ni}^{2+}}^b = \frac{1000c_0}{1000 + K_1c_{\text{NH}_3(aq)}} \]  

(16)

Aqueous ammonia is a weak base and therefore, in addition to the formation of complex ion \( \text{Ni(NH}_3)_2^{2+} \) with \( \text{Ni}^{2+} \), also partially dissociates into ammonium and hydroxide:

\[ \text{NH}_3(aq) + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^- \]  

(17)

where \( K_b \) is the base dissociation constant of aqueous ammonia.

Substituting \( 10^{p\text{H} - 14} \) for \( c_{\text{OH}^-} \times 10^{-3} \) and rearranging for \( c_{\text{NH}_3(aq)} \) gives

\[ c_{\text{NH}_3(aq)} = c_{\text{NH}_4^+} \times 10^{p\text{H} + pK_b - 14} \]  

(18)

Substituting Eq. (18) into Eq. (16) gives

\[ c_{\text{Ni}^{2+}}^b = \frac{1000c_0}{1000 + c_{\text{NH}_4^+} K_1 \times 10^{p\text{H} + pK_b - 14}} \]  

at pH < 9  

(19)

2.3. Overpotential

The overall overpotential \( \eta \) as a function of deposition time was obtained by measuring the system mixed potential, fitting the data, and subtracting nickel equilibrium potential. The mixed potential measurement was carried out in a plating bath consisting of 1 M NiSO\(_4\), 2.5 M NH\(_4\)F, and 0.2 g/L sodium dodecyl sulfate at pH 8 and 60°C. A piece of porous silicon of area 1.0 cm\(^2\) was immersed into the plating bath in a 50 mL PTFE (polytetrafluoroethylene) beaker as the working electrode. A saturated calomel electrode (SCE) served as the reference electrode and was placed in a saturated KCl solution which is connected with the plating bath via a saturation KCl salt bridge made of a polyethylene tube. The mixed potential of the PS in the plating bath was recorded using a Keithley multimeter. The resulting data are shown in Fig. 1(b); polynomial fitting of the data gives

\[ E_{MP} \quad (V \text{ versus SCE}) = -0.834 + 3.25 \times 10^{-5} t \]

\[ -1.36 \times 10^{-9} t^2 + 1.88 \times 10^{-14} t^3 \]  

(20)

The overall overpotential of nickel deposition reaction is [50]:

\[ \eta = E_{eq} - E_{MP} \]  

(21)

where \( E_{eq} \) corresponds to nickel equilibrium potential in 1 M NiSO\(_4\) + 2.5 M NH\(_4\)F and pH 8 solution. According to the Nernst equation, \( E_{eq} = -0.556 \) V (versus SCE).
with the diffusion of nickel ions. The deposition reaction proceeds with relative ease in comparison to the diffusion rate of nickel. A large \( \xi \) value indicates a non-uniform nickel deposition distributions.

2.4. Polarization parameter

A polarization parameter, which incorporates all the interfacial kinetics and diffusion parameters, can be defined to discuss the effects of these factors and variables on the concentration distribution and the deposition uniformity of nickel inside the pores [51]:

\[
\xi = \frac{r_0 R_p^0}{n F D_{Ni^{2+}} (c^{Ni^{2+}}_0)^{a_c F RT \eta_S}} \left[ \exp \left( \frac{\alpha_c F}{RT} \eta_S \right) - \exp \left( - \frac{\alpha_d F}{RT} \eta_S \right) \right]
\]  

(23)

where \( R_p^0 \) is an unit length which makes \( \xi \) a dimensionless parameter.

\( \xi \) can be regarded as the ratio of the interfacial reaction rate to the diffusion rate of nickel. A large \( \xi \) value implies that the interfacial deposition reaction proceeds with relative ease in comparison with the diffusion of nickel ions. \( \xi \) can be expressed as a product of two components, one being \( \zeta \), independent of time, the other being \( \phi \), involving the overpotential \( \eta_S \) which is a function of time. They are defined, respectively, as follows:

\[
\xi = \zeta \phi
\]

(24)

\[
\zeta = \frac{r_0 R_p^0}{n F D_{Ni^{2+}} (c^{Ni^{2+}}_0)^{a_c F RT \eta_S}} \left[ \exp \left( \frac{\alpha_c F}{RT} \eta_S \right) - \exp \left( - \frac{\alpha_d F}{RT} \eta_S \right) \right]
\]

(25)

\[
\phi = \exp \left( \frac{\alpha_c F}{RT} \eta_S \right) - \exp \left( - \frac{\alpha_d F}{RT} \eta_S \right)
\]

(26)

2.5. Effects of additive coumarin

The leveling mechanism of coumarin, as a typical leveler, was extensively studied \([48,49,55-59]\). Coumarin inhibits electrochemical deposition by adsorbing on depositing sites and thus reducing the area available for electrodeposition. It is consumed at the depositing sites and its surface coverage and hence its leveling actions are diffusion controlled provided that the surface feature size is on the order of diffusion boundary layer thickness, which is typically 1-100 \( \mu \)m, and the concentration of additive coumarin is small. It follows that the deposition at protrusions, which receive a higher flux of the leveler and have higher coverage, is more prohibited while deposition at recesses, receiving lower flux and having lower coverage of the leveler, is less prohibited, progressively leading to smooth deposits.

For the geometry in the present study, the pore depth is far greater than 100 \( \mu \)m. If the diffusion–adsorption leveling theory remains valid for such a depth, it would be likely to form a gradually decreasing coverage distribution of the leveling additive along the depth of the pores. As a consequence, the deposition of nickel would become more inhibited in the upper portion but less inhibited toward the pore bottom, compensating for its deposition non-uniformity due to depletion of nickel ions inside the pores and eventually leading to a uniform nickel deposition. We will evaluate this possibility by calculating the surface coverage of coumarin along the pore wall and the corresponding nickel deposition distributions.

Following Madore et al. \([49]\) and Roha and Landau \([55]\), the adsorption and consumption mechanism of coumarin is

\[
\text{adsorption and desorption coumarin} \rightarrow \text{(coumarin)}_{ads}
\]

consumption by cathodic reduction \((\text{coumarin)}_{ads} \rightarrow \text{products})

(27)

(28)

The rates of these processes are given by

\[
r_a = k_a \theta_C (1 - \theta_C)
\]

(29)

\[
r_d = k_d \theta_C
\]

(30)

\[
r_C = \theta_C k_C \exp (h_C \eta)
\]

(31)

where the surface coverage of coumarin and its consumption rate are denoted by \( \theta_C \) and \( r_C \), and subscript \( C \) represents additive coumarin. The adsorption and desorption of coumarin are assumed to be at equilibrium so that \( \theta_C \) is obtained by

\[
\theta_C = \frac{k_a c_i^C}{k_a c_i^C + k_d}
\]

(32)

Likewise, the concentration distribution of coumarin inside the pores is governed by Eq. (5), and the initial and boundary conditions Eqs. (6)–(10) also apply to coumarin with the rate term in Eq. (9) being replaced by Eq. (31).

In the presence of coumarin, nickel must compete with coumarin for available surface sites so that

\[
n_{Ni} = \frac{\xi}{n F} - D_{Ni^{2+}} \frac{c_{Ni^{2+}}^{b_c}}{R_p} \frac{\partial c_{Ni^{2+}}^{b_c}}{\partial r} = \frac{1 - \theta_C}{n F} \left( c_{Ni^{2+}}^{b_c} \right)^{\gamma} \left[ \exp \left( \frac{\alpha_c F}{RT} \eta_S \right) - \exp \left( - \frac{\alpha_d F}{RT} \eta_S \right) \right]
\]

(33)

The computation was performed in two steps. First, the coverage distributions of coumarin inside the pores under various bulk concentrations were derived. Second, the concentration distributions of nickel were solved by entering the resulting coumarin coverage distributions into Eq. (33) and substituting Eq. (33) for Eq. (11). Finally, from the resulting concentration distributions of nickel ions at various coumarin concentrations, corresponding nickel deposition rate distributions were calculated using Eq. (33).

Physical properties used for the numerical calculation are reported in Table 1.
Table 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>System values</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>(R_p) (m)</td>
<td>(5 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>(L_p) (m)</td>
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<tr>
<td>(\dot{P}) (s)</td>
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<td></td>
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<tr>
<td>(D_{Ni^{2+}}) (m²/s)</td>
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<td>[52]</td>
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<tr>
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<td>(c_\infty^{Ni^{2+}}) (mol/m³)</td>
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<td></td>
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<tr>
<td>(pK_b)</td>
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<td>(K_1)</td>
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<td>[54]</td>
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<td>(K = k_d/c_{Ni^{2+}}) (mol/m³)</td>
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<td>(b_e) ((V^{-1}))</td>
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<td>[57]</td>
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<tr>
<td>(k_{Ni^{2+}}) (mol/m² s)</td>
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<td>[57]</td>
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<tr>
<td>(D_{coumarin}) (m²/s)</td>
<td>(7.85 \times 10^{-6})</td>
<td>[57]</td>
</tr>
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</table>

Femlab, a finite element based solver, was employed for the computation in this study.

3. Results and discussion

In the following discussion, \(Ni^{2+}\) concentration and its deposition rate distribution refer to the ones along the depth of the pores at the pore wall.

3.1. Polarization parameter \(\xi\)

Since the magnitude of the polarization parameters \(\xi\) is determined by the dominance of surface kinetics or mass transport, the dependence of the \(Ni^{2+}\) concentration distribution and deposition uniformity on the interfacial kinetics and diffusion can be represented by variation of the value of \(\xi\). At a given value of \(\xi\), the solution composition, pH, and temperature are held constant, and the overpotential is also fixed. Under such conditions, it was found that the \(Ni^{2+}\) concentration profile reaches steady state within less than 1 min. Fig. 2 shows the steady state concentration distribution of nickel ions along the pore wall for different values of polarization parameter \(\xi\). For all the values of \(\xi\), nickel ion concentration decreases toward the pore bottom due to its consumption along its diffusion path. It is important to note that Fig. 2 illustrates the trend toward a more uniform distribution as the value of \(\xi\) is decreased. For a large value of \(\xi (>20 \times 10^5)\), which corresponds to a fast interfacial reaction relative to \(Ni^{2+}\) diffusion, the reaction is under diffusion control; the \(Ni^{2+}\) concentration inside the pores exhibits an extremely non-uniform distribution. As the value of \(\xi\) decreases, the distribution becomes more uniform because the dominating factors shift from concentration limitation to interfacial reaction resistance. When \(\xi\) decreases below \(1 \times 10^5\), the variation of \(Ni^{2+}\) concentration with the depth is very small or even negligible. The interfacial kinetics factor completely dominates the concentration distribution.

According to Eqs. (9), (11), and (23), the nickel deposition rate is

\[v_{Ni} = D_{Ni^{2+}}c_{Ni^{2+}}^{b} \xi (c^{*})^{1-\alpha c/n} \]  

(34)

By substituting the concentration distributions in Fig. 2 into Eq. (34), the deposition rate distributions corresponding to each \(\xi\) value in Fig. 2 were calculated and are shown in Fig. 3. In the calculation, the \(c_{Ni^{2+}}^{b}\) is taken to be 13.5 mol/m³, equivalent to a nominal concentration \(c_0\) of 1000 mol/m³. Fig. 3 indicates that the deposition distribution shows the same dependence on polarization parameter \(\xi\) as the \(Ni^{2+}\) concentration distribution in Fig. 2. The curves in Fig. 3 cross because with lowering the value of polarization parameter \(\xi\), deposition rate at the upper portion decreases while nickel ion concentration at the lower portion increases leading the deposition rate there to increase.

In summary, a large \(\xi\) value, corresponding to mass transfer limitations, leads to non-uniform distributions of \(Ni^{2+}\) concentration and deposition rate while, for a small \(\xi\) value, the deposition is dominated by the interfacial reaction kinetics; more uniform \(Ni^{2+}\) concentration distribution and thus uniform deposition profile can be expected. It follows that the strategy for obtaining a uniform nickel distribution inside the pores is to lower the value of polarization parameter \(\xi\) so that the deposi-
tion process shifts from mass transfer limitations to interfacial kinetics control.

3.2. Deposition time

The overpotential \( \eta_S \) involved in the polarization parameter \( \xi \) is the driving force for the nickel deposition reaction. However, the overpotential \( \eta \) and \( \eta_S \) are not constant through the deposition process. According to Eq. (22), the variation of \( \eta \) with deposition time is shown in Fig. 4.

The initial overpotential is about 0.28 V. Immediately following the initiation of the plating process, the overpotential declines rapidly until it reaches a plateau at about 0.015 V after about 5 h deposition. It was considered that the increasing coverage of the pore wall by nickel causes the decline of the overpotential [12]. The declined overpotential induces an exponential decrease of the deposition rate of nickel based on Eq. (11). By substituting Eq. (23) into Eq. (34), the deposition rate \( v_{Ni} \) was calculated and is also shown in Fig. 4. The calculation was performed assuming that the Ni\(^{2+}\) concentration inside the pores is equal to its bulk concentration, \( \zeta = 1750 \) (corresponding to the bath condition for the mixed potential measurement shown in Fig. 1(b)), and \( c_{b}^{Ni^{2+}} = 13.5 \text{ mol/m}^3 \). As can be seen, the deposition rate shows a dramatic decrease within the initial 1 h of deposition. Since the change in Ni\(^{2+}\) concentration inside the pores was not taken into account, the variation of the deposition rate in Fig. 4 is thus due solely to the decline in the overpotential. The reduced deposition rate corresponds to a decreased \( \xi \). This decrease in the polarization parameter \( \xi \), on the basis of the discussion in the section of polarization parameter, represents a shift of the controlling factor for the deposition uniformity from mass transfer to interfacial kinetics, and therefore a shift from the initial non-uniform deposition to more uniform one.

Fig. 5 shows the variation of Ni\(^{2+}\) concentration distribution with time as the result of the decline in the overpotential and the deposition rate. Fig. 6 shows the variation of the deposition rate distribution with time, which corresponds to the Ni\(^{2+}\) concentration distribution in Fig. 5. These two figures show the trend toward more uniform deposition with decreased overpotential and deposition rate. Initially, the Ni\(^{2+}\) concentration and deposition rate show a highly non-uniform distribution. The deposition occurs very fast and preferentially at the upper portion of the pores due to limited mass transport toward the pore bottom. As the deposition process continues, the mass transfer limitations are lessened because of the reduced deposition rate, and the Ni\(^{2+}\) concentration and deposition rate become more uniform. Eventually, a uniform deposition distribution is obtained.

3.3. Operating parameters

The non-uniformity of deposition at the initial stage can be remedied by controlling the time-independent factor \( \zeta \) of polarization parameter \( \xi \). \( \xi \) is a function of \( i_0 \), \( D_{Ni^{2+}} \), and \( c_{b}^{Ni^{2+}} \). Small \( i_0 \), large \( D_{Ni^{2+}} \), and high \( c_{b}^{Ni^{2+}} \) give a low \( \xi \) value, thus leading to a uniform deposition. Here the discussion is limited to the schemes to control the \( c_{b}^{Ni^{2+}} \) by bath chemistry such that \( \xi \) has a small value. The dependence of \( c_{b}^{Ni^{2+}} \) on \( c_0 \) and pH is given by Eq. (19). Substitution of Eq. (19) into Eq. (25) gives the
dependence of $\zeta$ on $c_0$ and pH:

$$\zeta = \frac{i^0 R_0 (1000 + c_{NH_4^+}) K_1 \times 10^{pH + pK_b - 14} \alpha c/n}{n FD_{Ni^{2+}} (1000 c_0) \alpha c/n (c_{Ni^{2+}}) 1 - \alpha c/n}$$  \hspace{1cm} (35)

From Eq. (35), the plots of $\zeta$ versus $c_0$ and pH are obtained and shown in Fig. 7. It shows that $\zeta$ value can be reduced effectively by increasing $c_0$ and lowering bath pH, and low bath pH is more effective in reducing $\zeta$ value. Therefore, more uniform deposition is expected when low pH plating bath with high Ni$^{2+}$ concentration is used.

### 3.4. Additive coumarin

Fig. 8 corresponds to the coumarin surface coverage distribution from the pore mouth to bottom at various coumarin bulk concentrations. The computation was performed assuming that the plating bath remains to be the solution consisting of 1 M NiSO$_4$, 2.5 M NH$_4$F, and 0.2 g/L sodium dodecyl sulfate at pH 8 and 60 °C. It is important to note that coumarin exhibits a declining coverage toward the pore bottom. As coumarin concentration is increased, such a profile moves toward the bottom, and the coverage at the upper portion becomes progressively higher. Fig. 9 shows the variations of nickel ion concentration distribution at deposition time of 5 min in the presence of coumarin corresponding to the coverage distribution in Fig. 8. It is obvious that the adsorption of coumarin at the pore wall alters the Ni$^{2+}$ concentration distribution through inhibition on nickel deposition. The Ni$^{2+}$ concentration is increased and its distributions become less non-uniform with the increase in coumarin concentration. This is because the inhibition of nickel deposition at the upper portion allows more nickel ions to diffuse to the lower portion.

Fig. 10 shows the rate distribution of nickel depositions in the presence of coumarin corresponding to the concentrations shown in Fig. 8. The calculation takes into account both...
the inhibiting effect of coumarin, which is proportional to its coverage shown in Fig. 8, and the resulting variations of Ni\(^{2+}\) concentration distribution shown in Fig. 9. The deposition becomes more uniform as more coumarin is added to the solution. The nickel deposition rate at the upper portion is significantly reduced with increased coumarin coverage, while the lower portion receives more deposition due to increased Ni\(^{2+}\) concentration.

3.5. Comparison with other plating processes for similar geometries

There is a geometrical similarity between the porous silicon and other geometries such as through-holes, vias, and trenches. Nevertheless, the nature and dependence on bath chemistry and operating variables of the plating processes for these geometries are significantly different. In the case of copper plating of through-holes, the ohmic resistance rather than mass transport dominates the plating uniformity [21,26]. In contrast, mass transport becomes significantly important in plating distribution of vias and trenches due to their closed end nature, and the potential field also contributes to the non-uniform vias plating profile [20]. For nickel displacing deposition into porous silicon in the present study, there is no potential field factor but mass transport becomes critically important because of the active sidewall of the PS and ultrahigh aspect ratio. The nickel distribution inside the pores is determined by a polarization parameter, the ratio of the surface reaction rate to the diffusion rate, which is similar to plating into a trench [51] and through-hole plating under mass transport control [22]. Improvement of nickel deposition uniformity can be made by lowering the value of the polarization parameter, such as, increasing nickel ion concentration and lowering bath solution pH. The shift of deposition process from being governed by restricted diffusion to surface reaction control is identified only in the displacement deposition of present study that favors uniform nickel distribution. Additives are shown to be effective in enhancing plating uniformity for all the geometries under certain conditions.

4. Conclusions

A model has been derived to describe the displacement deposition of nickel into porous silicon with an ultrahigh aspect ratio. It is shown that the deposition distribution along the pore depth exhibits a strong dependence on the polarization parameter \(\xi\), a measure of interfacial reaction rate compared to diffusion rate. High values of \(\xi\) correspond to a situation where the deposition distribution tends to be highly non-uniform as diffusion controls the deposition at the lower portion of the pores. On the other hand, a small value of \(\xi\) is associated with uniform deposition distribution inside the pores. Non-uniform deposition primarily occurs at the initial stage in which the reaction is accompanied by a high overpotential as the driving force for the deposition reaction. As the deposition process continues, the deposition rate drops to a low value, and the deposition distribution shifts from Ni\(^{2+}\) diffusion control to its interfacial reaction dominance. Consequently, a uniform Ni\(^{2+}\) concentration and deposition rate distribution results. It is predicted that the non-uniformity at the initial stage could be remedied by increasing the bulk concentration of nickel ions and decreasing plating bath pH. Adding inhibitive additive coumarin to the plating solution is shown to promote the uniformity of the deposition distribution.

Appendix A. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b_C)</td>
<td>Tafel constant of coumarin cathodic reduction (V(^{-1}))</td>
</tr>
<tr>
<td>(c)</td>
<td>concentration (mol/m(^3))</td>
</tr>
<tr>
<td>(c_0)</td>
<td>nominal Ni(^{2+}) concentration (mol/m(^3))</td>
</tr>
<tr>
<td>(c_C)</td>
<td>surface concentration of coumarin at the substrate (mol/m(^3))</td>
</tr>
<tr>
<td>(c_{Ni^{2+}}^\infty)</td>
<td>Ni(^{2+}) concentration corresponding to its exchange current density (mol/m(^3))</td>
</tr>
<tr>
<td>(D)</td>
<td>diffusion coefficient (m(^2)/s)</td>
</tr>
<tr>
<td>(E_{eq})</td>
<td>equilibrium electrode potential of Ni(^{2+}/Ni), V (versus SCE)</td>
</tr>
<tr>
<td>(E_{MP})</td>
<td>mixed potential of the displacement deposition system, V (versus SCE)</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday’s constant, 96,487 C/mol.</td>
</tr>
<tr>
<td>(i)</td>
<td>current density (A/m(^2))</td>
</tr>
<tr>
<td>(i^\Phi)</td>
<td>Ni(^{2+}/Ni) exchange current density (A/m(^2))</td>
</tr>
<tr>
<td>(k_a)</td>
<td>adsorption rate constant of coumarin (m/s)</td>
</tr>
<tr>
<td>(k_c)</td>
<td>cathodic reduction rate constant of coumarin (mol/m(^2) s)</td>
</tr>
<tr>
<td>(k_d)</td>
<td>desorption rate constant of coumarin (mol/cm(^2) s)</td>
</tr>
<tr>
<td>(K_b)</td>
<td>base dissociation constant of aqueous ammonia</td>
</tr>
<tr>
<td>(K_n)</td>
<td>stability constant of Ni(NH(_3))(_n^{2+})</td>
</tr>
<tr>
<td>(L_p)</td>
<td>pore depth (m)</td>
</tr>
<tr>
<td>(n)</td>
<td>amount of electrons transferred when 1 mol of Ni is deposited (mol)</td>
</tr>
<tr>
<td>(r)</td>
<td>radial distance from the center axial line in the pore (m)</td>
</tr>
<tr>
<td>(r_a)</td>
<td>adsorption rate of coumarin (mol/m(^2) s)</td>
</tr>
<tr>
<td>(r_C)</td>
<td>cathodic reduction rate of coumarin (mol/m(^2) s)</td>
</tr>
<tr>
<td>(r_d)</td>
<td>desorption rate of coumarin (mol/m(^2) s)</td>
</tr>
<tr>
<td>(R)</td>
<td>universal gas constant, 8.314 J/mol K</td>
</tr>
<tr>
<td>(R^0)</td>
<td>initial pore radium (m)</td>
</tr>
<tr>
<td>(R_p)</td>
<td>unit length (m)</td>
</tr>
<tr>
<td>(t)</td>
<td>time (s)</td>
</tr>
<tr>
<td>(t^\Phi)</td>
<td>total depositing time (s)</td>
</tr>
<tr>
<td>(T)</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>(v)</td>
<td>deposition rate (mol/m(^2) s)</td>
</tr>
<tr>
<td>(y)</td>
<td>axial distance from the pore mouth (m)</td>
</tr>
</tbody>
</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_C)</td>
<td>apparent transfer coefficient</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>concentration dependence exponent of the exchange current density</td>
</tr>
<tr>
<td>(\xi)</td>
<td>time-independent factor of polarization parameter</td>
</tr>
<tr>
<td>(\eta)</td>
<td>overpotential (V)</td>
</tr>
<tr>
<td>(\theta_C)</td>
<td>surface coverage of coumarin at the substrate</td>
</tr>
<tr>
<td>(\xi)</td>
<td>polarization parameter</td>
</tr>
<tr>
<td>(\phi)</td>
<td>time dependent factor of polarization parameter</td>
</tr>
</tbody>
</table>

The inhibiting effect of coumarin, which is proportional to its coverage shown in Fig. 8, and the resulting variations of Ni\(^{2+}\) concentration distribution shown in Fig. 9. The deposition becomes more uniform as more coumarin is added to the solution. The nickel deposition rate at the upper portion is significantly reduced with increased coumarin coverage, while the lower portion receives more deposition due to increased Ni\(^{2+}\) concentration.
References